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THE OSMOTIC PRESSURE AND THE DEPRESSION OF THE FREEZING POINTS OF SOLUTIONS OF GLUCOSE.¹

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PART I.²

In a previous communication³ we described certain "thermometer effects," or "temporary fluctuations of pressure which follow changes of temperature and are due to the expansion or contraction of the liquids in the cell, and not to actual variations in osmotic pressure," and we announced our intention of eliminating these troublesome phenomena by working, in the future, at constant temperatures, or at temperatures so nearly constant that the passage of water through the membrane can keep pace with the expansion and contraction of the contents of the cell.

¹ The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution.

² Our measurements of the osmotic pressure of solutions of glucose are not yet as numerous as we desire to make them before publishing the results, the work having been delayed by difficulties, some of which are explained in the present paper. The reason for dividing the account of the work and publishing the first part at the present time is a desire, on our part, to make clear, without unnecessary repetition, the conditions under which another investigation was prosecuted, namely, *the redetermination of the osmotic pressure of cane sugar solutions*, an account of which is given in the following paper.

³ THIS JOURNAL, 34, 23, 92.

These "thermometer effects" were the most serious obstacles with which we had to contend in our attempt to secure accuracy in the measurement of pressure, and the means which we have since employed to reduce them to harmless proportions are quite elaborate. In general they consist of: (1) A large and well protected bath containing over 300 liters of water, which is kept in constant motion; (2) a nearly tight enclosure over the bath, the air in which is kept in constant circulation through pipes lying in the water below; and (3) various automatically regulated electric and gas stoves, which serve to maintain uniform temperature conditions outside the bath.

The bath is a rectangular wooden box 1.23 meters in length, 0.45 meter in width and 0.65 meter in depth which is lined with copper. Its total capacity is 360 liters, while the space occupied by the water is about 300 liters. This tank, or bath, is surrounded by a larger wooden box of such dimensions that the distance between them is not less than 75 mm. at any point, and the intervening space is tightly packed with hair.

The house above the tank has a height of 0.5 meter, a width equal to, and a length about three-fourths, that of the bath. It is provided with a top, or cover, which is hinged at the back, and is opened or closed by means of a cord running over stationary pulleys on the ceiling above. It is also provided in front with a mirror plate-glass window, which is hinged at the bottom. The bath, with the house above, rests upon heavy brackets, which are built into the thickest and most stable of the masonry walls of the laboratory. The same is true of the cathetometer and the standard scale which are employed in the measurements. These instruments, like the bath itself, rest upon supports which are independent of the floor or other woodwork of the building.

The cells, when a measurement is in progress, are located in the bath at a depth considerably below the surface of the water, while the portions of the ascending limbs of the manometers which contain the air are in the house above. Hence the liquids in the cell tend to take the temperature of the

water, and the gas in the manometers, the temperature of the air above. It is, therefore, important (1) that the temperature of the water and of the air within shall be kept nearly constant, and (2) that the temperature of the air shall not differ greatly from that of the water.

Since the trustworthiness of our results is measured solely by the excellence of the method by which they were obtained, and nothing should be taken for granted on that score, we shall not hesitate to describe the details of our present arrangements. These details are seen in the accompanying figures.

Fig. I. is a longitudinal section through the middle of the

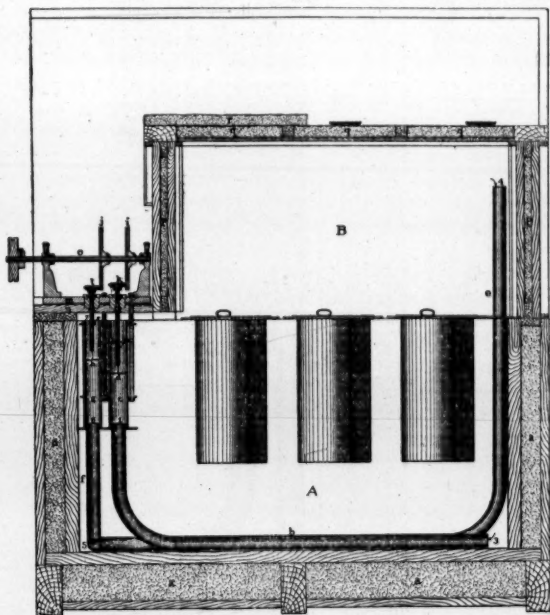


Fig. I.

bath. A is the water tank and B the house, covering about three-fourths of it. The hair packing between the tank and the box is designated by the letter *a*. The lead pipe *b* (see also Fig. II.), which has an internal diameter of 30 mm., lies upon the bottom of the tank and enters the larger brass pipe *c* at 1. The brass pipe *c* is provided with a series of holes extending entirely around it at 2, Fig. 1A, which is below the

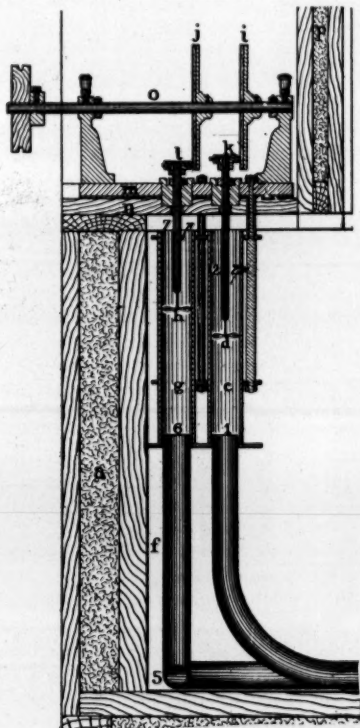


Fig. 1A.

level of the water in the tank. By means of the propeller *d*, the water is constantly drawn into the lead pipe at 3 and delivered through the holes at 2 in the brass pipe. In this manner, with the propeller running at a moderate rate, a uniform temperature is secured throughout the whole body of the water, so uniform, in fact, that differences cannot be detected with the thermometers graduated to $0^{\circ}.1$.

The two lead pipes, through which the air in the house above the tank is drawn, are of the same size as that through which the water is pumped. One of these, *e* Fig. I. (see also Fig. II.), is shown in the background. Starting at 4, at the rear right-hand corner, it passes downwards through the water and then along the angle made by the bottom and back of the tank to the other end, where it curves and enters the vertical pipe *f* at 5. At this point it meets the other air pipe *e'* (see Fig. II.), which is identical with it except that the latter occupies the opposite side of the bath. The vertical pipe *f*, which serves as a junction for the two air pipes *e* and *e'*, like the water pipe, enters a larger brass pipe *g* at 6, which extends to some distance above the surface of the water. By means of the rotating fan *h*, the warmer air in the upper part of the house is constantly drawn through the pipes *e* and *e'*, lying in the water, and is delivered again at 7 above the surface at the other end of the tank. The air in the house is thus kept in circulation, and at a uniform temperature which cannot rise much above, or fall much below, that of the water in the bath. The magnitude of the difference between the temperature of the air and that of the water will depend, of course, upon the rapidity of the circulation of the former through the submerged pipes, *i. e.*, upon the efficiency and speed of the fan, also upon the tightness of the house and the frequency of opening it for the purpose of introducing or removing cells.

The machinery by which the pump *d* and the fan *h* are rotated is located above the tank at the left (see Fig. IA), and outside the house. It consists, essentially, of the two rotating disks *i* and *j*, which drive the pump and fan pulleys *k* and *l*. Both the disks and the pulleys are faced with sole leather, and the facings of the former are so trimmed on the

lathe that they increase slightly in thickness from the center outward. The advantage of giving this form to the disk face is obvious. The friction between it and the pulley remains constant, since any wearing away of the running surfaces is automatically compensated by a drop of the pulley. The speed of the pumps can be regulated at will, within large limits, by adjusting the pulleys to run at different distances from the centers of the disks. The gradual descent of the pulleys to compensate for wear is attended by an increase of speed, but the effect is small since the drop does not amount to more than 1 mm. per month of constant running. The iron bed plate *m* is raised above the wooden tank cover *n* by thick strips of asbestos board, thus providing for ventilation. A further precaution against communicating to the bath the small amount of heat developed by the machinery consists in placing two small fans (not shown in the figure) upon the shaft just above the pulleys.

In the first bath built by us, the air compartment covered the whole tank, and the disks and pumps were inside and the motor and driving pulley outside the house. This arrangement was, however, found to be a bad one, owing to the high speed which had to be given to the fan in order to keep the temperature of the air near that of the water.

As now arranged, the machinery runs smoothly and with little noise. The heat developed by it does not sensibly affect the temperature of the bath. The air-fan is made to rotate about 2500 times per minute, and the water pump about 800 times.

It is essential in a bath of this kind that the enclosure above the water shall be as nearly air-tight as it is possible to make it. This condition has been realized in our apparatus to a satisfactory degree by selecting thoroughly seasoned lumber for its construction, by setting all tongues of the woodwork in their grooves with an elastic varnish, by embedding strips of insulating tape in varnish over all joints, and, finally by enameling heavily the whole interior of the house. The hinged top and the plate-glass window in front close, at all points on the inside, against rubber weather strips, and the cracks upon

the outside are covered with strips of insulating tape, which is usually sticky enough to adhere firmly to the wood, but is easily removed whenever the bath is to be opened at the top or in front.

The house, as well as the tank, has double walls, except in front and on the top, and the spaces between the walls are filled with hair as seen at *p* in Fig. I. The spaces in the framework of the top *q, q, q*, are filled with hair, which is held in place by a covering of flannel tacked to the frame. Finally, the whole top of the house is covered by the hair mattress *r*. The glass of the window in front is completely covered by a thick flannel-encased pad of hair, which is divided at various points, from the upper edge towards the bottom, thus providing numerous narrow curtains, any one of which may be lowered for the purpose of reading a manometer or thermometer without exposing more than a very small portion of the glass of the window, the light necessary for the illumination of the instrument being thrown in from the outside.

However great the fluctuations of temperature outside the bath, the changes in the temperature of the large body of water within are necessarily very slow. The effect of external conditions upon the temperature of the enclosed air space is more marked. A considerable rise or fall on the outside is soon followed by a small corresponding change in the temperature of the air above the water, but such fluctuations are not large or of long duration, even under the most unfavorable conditions, owing to the continuous and rapid circulation of the air through the submerged pipes. The rate of this circulation can, of course, be increased, if desired, by raising the speed of the fan.

Fig. II. presents a view of the tank as seen from above, and serves to explain the internal arrangements for the accommodation of the cells and also some of the features of construction which have already been pointed out.

The water and air pipes are seen, the former at *b* and the latter at *e* and *e'*. The hair packing between the tank and the exterior box is designated at various places by the letter *a*.

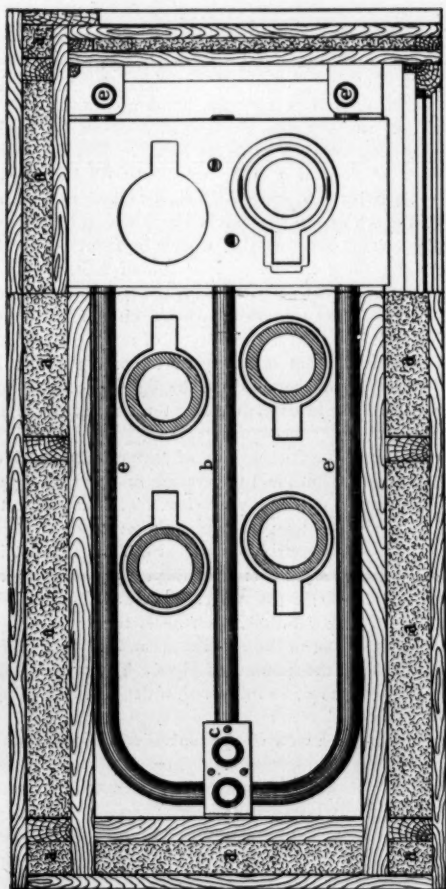


Fig. II.

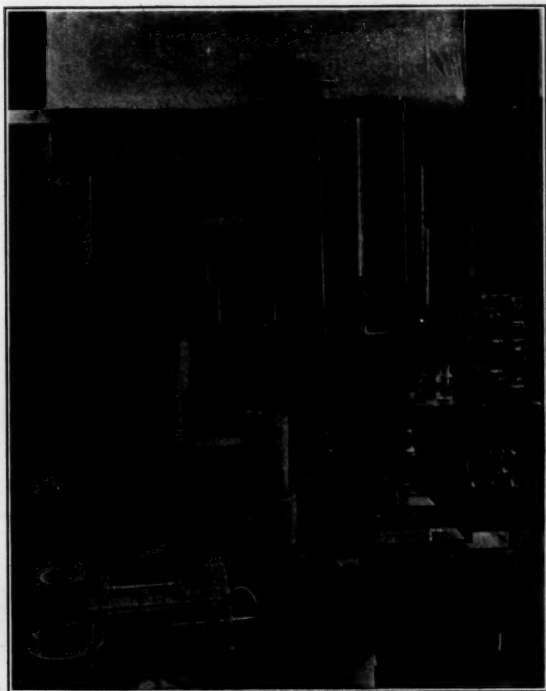


Fig. III.

There is also seen at the right in Fig II. one of the three iron plates which rest upon the edges of the tank (see also Fig. III.) and serve to hold in place the six galvanized iron cans (*a* Fig. III.), in one of which the cell is placed when a measurement is to be made. Each plate is perforated for the reception of thermometers, which give the temperature of the water in the bath.

The cans, *a* Fig. III., have a depth of 0.4 meter and a width of 0.15 meter, and are provided on one side with a rectangular extension for the accommodation of the long vertical limbs of the manometers. To weight the cans in the water, and at the same time to facilitate an even distribution of heat, heavy cast-iron cylinders (*b* Fig. III.) are employed. These cylinders, weighing each about 8 kilograms, are placed in the cans, and the bottles containing the cells rest upon the bottoms of the latter within the former. The can *a*, the iron cylinder *b* and the bottle for the cell are seen in their respective positions and correct relative proportions in Fig. IV. The open end of the can is plugged with hair while a measurement of pressure is in progress, in order that the cell contents may more surely acquire the temperature of the water, and the air in the manometer that of the house above.

Fig. III. is a photograph of the bath in an unfinished condition, together with certain accessories which will be described later. The hinged cover of the bath, stripped of its upholstery, is shown at *d*, *e* is the plate-glass window without its curtain, *f* is the cathetometer, and *g* the standard scale. Within the bath are seen parts of the vertical portions of the air pipes (*i* and *h*), the iron plates, the upper ends of some of the cans, and the usual arrangement of the thermometers; while to the left, on the outside, is shown the machinery by which the water and air pumps are driven. It is to be stated with regard to the thermometers used in the bath that they are all graduated to $0^{\circ}.2$, and that the errors of each have been determined by comparison with a thermometer which has been tested at the "Reichsanstalt."

The only remaining feature of the bath which requires explanation is the automatically regulated electric stove, which

was devised for the purpose of raising and maintaining the

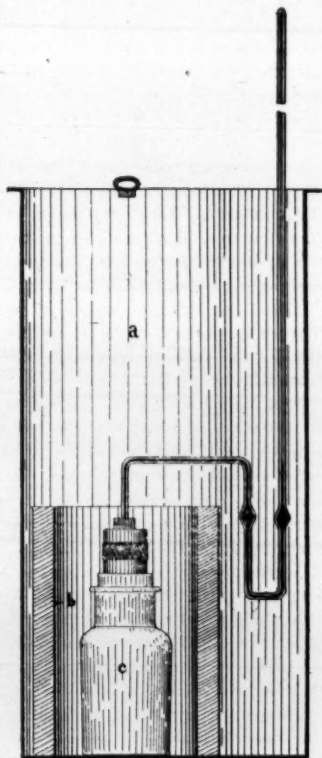
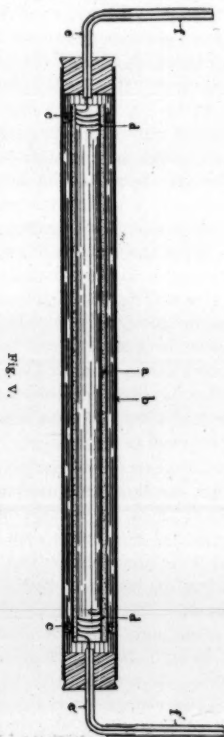


Fig. IV.

temperature of the water whenever it is desired to secure measurements of pressure at higher temperatures than those

prevailing outside the bath. The stove in question is shown in Fig. V. It consists of the porcelain tube *a*, which has a



length of 625 mm. and a diameter of 30 mm. and the enamel-
elled steel tube *b*, which is separated from *a* by the asbestos
rings *c*, *c*. The ends of the porcelain tube are silvered for a

short distance, both externally and internally, and the outside is graphited by the method previously described by Morse and Frazer.¹ Electrical contact is secured by the expanding spring wire coils d, d , which are inserted in the ends of the porcelain tube and press against the silver lining. The ends of the steel tube are closed with rubber stoppers, through which pass the short bent glass tubes e, e' . The leads to the battery are protected from the water by the rubber tubes f, f , which fit the wires so loosely that air can readily pass in either direction. The stove lies on the bottom of the tank, with the leads extending upwards through the water and out of the bath at one end. It is connected with a 74-volt battery and yields, with no external resistance in the circuit, and at about 20° , 50,000 calories per hour. When the stove is in use it is necessary to give the pumps a somewhat higher speed than is otherwise required in order to secure uniform temperature conditions. The stove circuit passes through a relay which is automatically operated by a sensitive thermostat placed in the water of the bath. The thermostat will be described later. We have had, up to the present time, but little occasion to use the bath stove because most of our measurements have been at temperatures which could be secured and maintained without its aid.

With a bath so well protected and containing so large a body of water, and capable, therefore, of absorbing or yielding up so much heat without any great change of temperature, we should have accomplished our object—the elimination of thermometer effects—had it not been for the fact that our building is heated only during the working hours of the day, *i. e.*, about 8 hours in the 24. The variations of temperature outside the bath were, accordingly, large, amounting frequently, in the winter months, to 25° . Even with so wide differences in the external conditions, the temperature changes in the water were very slow. These changes were twofold and characteristic. They consisted in a slight rise, during the daytime, above what may be called an equilibrium temperature, and a slight fall below it at night, and, at the same time, a slow but

¹ THIS JOURNAL, 33, 93.

continuous change in the temperature of the water, which was, in general, upwards or downwards, according to the season.

The effect of the large daily fluctuations of temperature outside the bath upon the temperature of the air within the manometer house was much more marked, and the highest speed of the air pump did not suffice to reduce the temperature differences of water and air to what we considered tolerable limits. Hence measures were taken to secure more uniform temperature conditions in the room in which the bath is located, and, since some of the appliances which were devised for this purpose are of a generally useful character, we shall describe them.

First of all, the bath was enclosed by a structure—3.3 meters in length, 2 meters in width, and 2.6 meters in height—which consists of a wooden framework, covered on both sides with thick muslin. The cloth upon the vertical walls was sized with gelatin to render it less pervious to air without interfering too greatly with the light, while that upon the roof was both sized and painted. The distance between the cloth sides is everywhere about 50 mm. The structure is provided with two doors of the same construction as the rest of the walls, also with windows at convenient points, which may be opened for the admission of daylight when it is desired to avoid the heat of electric lamps, *e. g.*, when the calibration of a manometer is in progress.

The space thus enclosed is maintained throughout the night at nearly constant temperature by an electric stove, which is controlled through a relay by means of a thermostat. The stove which is seen at *n* in Fig. III., is a terra cotta cylinder 300 mm. in height and 150 mm. in width. It is graphited externally by the method previously described¹ by Morse and Frazer and develops, when connected with the 74-volt battery, 250,000 calories per hour.

The relay which is used in connection with the stove is seen at *k* in Fig. III. It is of the common "pony" type which is employed on short telegraph lines, with provision, however,

¹ THIS JOURNAL, 32, 93.

for the prevention of sparking when the stove circuit is opened or closed by the thermostat.

The mercury thermostat, which is employed to control the stove circuit, is shown in Fig. VI., and again at *j, j, j* in Fig. III. It is the instrument which we use to control the temperature of all kinds of laboratory baths, whether they are heated by electricity or by gas.

The principal objection to electric mercury thermostats is the sparking which occurs at the closing and, particularly, at the breaking of the circuit. The surface of the mercury and the interior of the glass tube soon become fouled with oxide, and the instrument is thereby rendered unreliable. The practice of covering the end of the mercury column with a layer of non-conducting non-oxygen absorbing oil is an unsatisfactory remedy because it results, especially in sensitive thermostats, *i. e.*, in those having narrow tubes, in a breaking of the column. The method of preventing sparking which we employ, and which we have found to be quite effective, consists in spanning the spark gap with a resistance which has a certain relation to the potential of the battery.

Fig. VI. represents the thermostat. It resembles the Reichardt thermostat for gas, and most of the electric thermostats which we have in use in the laboratory are, in fact, transformed Reichardt instruments. The brass rod *a* passes through the cork and is terminated by a platinum tip. It is connected through the wire *c* with the binding post *b*, which, in turn, is connected with the resistance *R* by the wire *d* and with the coils of the relay by the wire *e*. The adjusting screw *f*, on the other hand, is connected by the wire *h* with the binding post *g*, which is connected, in its turn, with the resistance *R* by *i*, and with the battery by *j*. The coil spring of brass wire *k*, by pressing the screw *f* outward, gives a surer electrical connection and a more permanent adjustment of the mercury. It also tends to prevent leakage of mercury along the screw thread.

For use in a room, or any other large space where the whole of the thermostat is within the enclosure, the instrument, including binding posts and resistance, is mounted on a board

which may be attached by screws to the wall or to any other

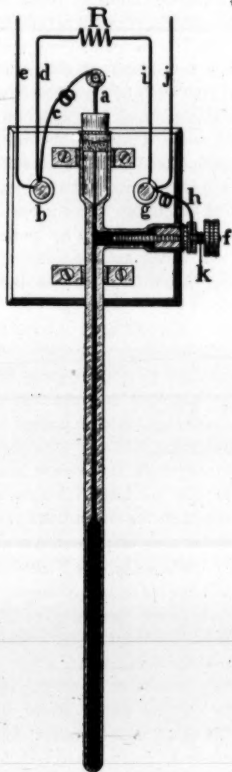


Fig. VI.

suitably located permanent object. If, on the other hand, only

the bulb of the instrument is to be immersed, as in a water or ordinary hot-air bath, the binding posts *b* and *g* are screwed into a small wooden block, which is bored through the center and firmly attached to the stem just under the side tube. Obviously, if a close regulation of temperature is required, in cases where only the bulb of the thermostat is within the heated space, the capacity of the side tube should be very small as compared with that of the bulb. This important point is usually overlooked by the makers of such instruments.

The relation of the resistance *R* to the potential of the battery requires careful attention. We use with each thermostat a single portable storage cell. The potential is, therefore, about 2 volts at all times, and the resistance, which wholly suppresses sparking in our instruments, is 200 ohms. This is just about the resistance of the *cold* filament of a 75-volt 16 candle-power lamp. Accordingly, a lamp of that rating is inserted in the shunt around the spark gap. With this relation of resistance to potential no sparking can be observed and the thermostats, if the mercury is pure and properly protected against dust, give satisfactory continuous service for several months without cleansing.

Since the circuit through the shunt is always closed, this method of suppressing sparking involves a waste of current while the circuit through the thermostat is open, but the loss amounts to only about 0.01 ampere and is quite insignificant.

The same device is employed to diminish sparking in the relay. The gap is shunted through lamps. Owing, however, to the comparatively high pressure of the battery for the stove, it is impracticable wholly to suppress the sparking, though it can readily be reduced to a tolerable limit, *e. g.*, to that which is usually observed in a relay on a telegraph line. The fraction of the current which flows continuously around the spark gap of the relay is not wasted, as in the case of the thermostat, because it necessarily contributes its proportion to the heat which is required to maintain the temperature of the room. It is hardly necessary to state that, in preparing a relay for use in a stove circuit, the usual position of the stops of the instrument must be reversed.

During the cold weather of the winter, the tax upon the battery which was necessary in order to maintain the temperature of the enclosure about the bath was inconveniently heavy. Accordingly, we determined to aid the electric stove by heating the outer room at night with a gas stove; and it was desirable that the latter, like the former, should be subjected to automatic regulation. The outcome was an electric gas regulator, controlled by an electric thermostat, which proved so satisfactory that we now use it for all kinds of baths heated by gas.

The gas stove is seen at *l* in Fig. III. Its construction is sufficiently obvious, and the only points to which attention will be called are the steel plate covering the stove and the cast-iron disk resting upon it. The former serves to protect the flames from air draughts, and the latter, to moderate—by continuing to radiate surplus heat, the fall of temperature which succeeds the partial shutting off of the gas supply. Only one of these disks is shown in the figure, but in cold weather a larger number of them can be employed with advantage.

The thermostat which is used to control the gas supply differs in no respect from that which is employed to regulate the electric stove. It is placed beside the thermometer, which is located, of course, with a view to ascertaining, as nearly as possible, the mean of the temperature conditions of the room.

The gas regulator is seen at *m* in Fig. III., and in Fig. VII. The soft iron tube *a*, Fig. VII., serves as a magnet core to raise and release the iron ball *b*, and thus to control the flow of gas through the regulator in the direction of the arrows. The ends of the core are slightly countersunk to furnish a seat for the ball, and the flaring sides of the openings are grooved to provide passages for a small amount of gas around the ball when it is in its place at the end of the tube. The brass tube *c* has an internal diameter quite exactly equal to that of the ball, so that the latter is always correctly guided to its proper position when the circuit through the coils of the magnet is closed by the thermostat. The internal wall of *c* is grooved longitudinally to a depth which will permit an abundant sup-

ply of gas to pass the ball. The ball rests upon the open brass wire spring *d*, which may, with advantage, have a considerable length and should not be made of very stiff wire. The

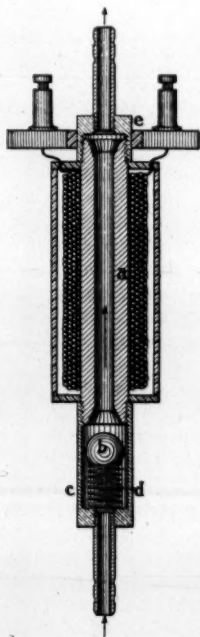


Fig. VII.

other end of the core is furnished with the brass tube *e*, which is shorter than *c* and not grooved internally; *c* and *e* are interchangeable.

The winding of the magnet should, of course, be with refer-

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ence to securing the longest life for the battery which is consistent with the efficient working of the instrument. All of our magnets are wound to a resistance of 20 ohms, and the portable storage cells which are used with them have a capacity of 50 ampere hours; accordingly, a single charge of a cell should suffice—excluding unavoidable waste—for 500 hours' continuous use of a regulator. But, since the discharge is intermittent, the endurance of the cell may be greater. Having determined what resistance a magnet is to have, the selection of the size of the wire to be used will, of course, depend on the manner of winding, *i. e.*, whether a single wire or several in parallel are to be employed. In any case the result sought will be to secure the largest number of turns in close proximity to the core which is consistent with the limiting conditions.

The circuit through the shunt to the spark gap in the thermostat is always closed, but, since this circuit also includes the magnet, its resistance is not less than 220 ohms, and the waste of current is therefore small.

Considered simply as a magnet and from the standpoint of efficiency, the regulator here described has obvious defects, but in order to utilize more fully than we have done the magnetic effects, it would be necessary to construct a much more complex and costly instrument.

The gas regulator, the battery, and the thermostat are connected in series, and, in order to reduce to a minimum the work to be done by the magnet, the regulator is fixed in an inclined position, as shown in Fig. III. The inclination given to it is such that the highest pressure of the gas (aided by the spring and the slightly magnetized condition of the core, which is due to the small current flowing continuously through the thermostat and magnet coils) will not quite suffice to raise the ball.

The arrangements for the regulation of temperature, which because of the importance of their purpose have been described at length in the foregoing pages, have been found entirely adequate. The "*thermometer effects*," which gave us so much concern while engaged in the measurement of the os-

otic pressure of cane sugar solutions, do not, under present conditions, manifest themselves.

It may be of interest to know within what limits the various appliances are effective, and these can be stated with a fair degree of precision. The temperatures of the larger room, which is heated by gas, and of the smaller one, which is heated by electricity, are recorded at regular intervals four times each night by the watchman. The records extend over several months and show fluctuations during the night, in winter, not exceeding 1° in the outer room and $0^{\circ}.5$ in the inner one. The usual fluctuations during the night are less than $0^{\circ}.6$ in the former and $0^{\circ}.25$ in the latter. These statements relate to the temperature at night only. Whatever difficulty we have had in the regulation of temperature has been due to the frequent overheating of the building during the day. The change in the temperature of the water of the bath, which is produced by an occasional overheating of the building, is, however, not sufficiently great or rapid enough to produce sensible thermometer effects in the cells.

Another difficulty which was encountered in our earlier work was the uncertainty regarding the true volume of the upper end of the manometer in the region where the form of the tube is altered in closing it. As stated in the published account¹ of that work, the form at this point was assumed to be spherical or conical according to its appearance, and the errors resulting from such an assumption were probably small except, perhaps, in the case of concentrated solutions. The doubt concerning the exact form of the end was not the only uncertainty introduced by the operation of closing the tube. The heating of the glass may well have been followed by changes of caliber farther down the manometer, as far down, in fact, as the heating effects of the flame extended. These changes of caliber, if they occur, are analogous to those observed in a thermometer bulb after heating, but in the case of a manometer there is no possible way of discovering their magnitude, since the calibration precedes the closing of the instrument.

¹ THIS JOURNAL, 34, 11.

Again, it is often difficult to locate with certainty the upper end of a fine tube, especially when the glass walls are thick and the form of the end is spherical or conical. There is the liability that the point sought will be slightly displaced owing to lack of parallelism between the inner and outer surfaces of the tube, and the fact that the surfaces in the region in question are not perpendicular to the line of vision. After finishing the first series of measurements on cane sugar solutions, we attempted to ascertain how far errors of reading from this source had entered into the work. A fine needle with a sharp point was fixed in a vertical position in the usual place of a manometer, and its length was determined by means of the telescope and the standard scale. The upper end of the manometer was then cut off and the detached tube placed over the needle, after which its length was again determined. The results were reassuring, since we could in no case detect a measurable difference between the length of the naked needle and its apparent length when covered by the tube.

In an earlier communication¹ we stated that Professor Abegg had kindly called our attention to an effective remedy for the uncertainties connected with the form of the closed end of the manometer—that of filling it with mercury, but that we had not, up to that time, succeeded in applying it to our satisfaction, owing to the difficulty of separating from the main column the necessary portion of mercury and of dislodging all the air from the space which it should fill completely. The much desired result has since been accomplished in an easy and entirely satisfactory manner, as follows:

After calibration, and when it is to be filled, the upper open end of the manometer is attached to a two-way stop-cock with one of its passages leading to a supply of mercury and the other to the supply of purified air.² When the air has been drawn into the manometer for the last time, a small quantity of mercury is allowed to follow it and close the tube. If the quantity which has been admitted is too large or too small, it can readily be readjusted by manipulating the reservoir and the stop-

¹ THIS JOURNAL, 34, II.

² *Ibid.*, 34, 9.

cock. The reservoir is then lowered until a large part of the air is in the bulb upon the vertical limb and the mercury plug which imprisons it is at a considerable distance from the top. The upper end of the tube is then drawn out to a finer one with thin walls, and the mercury plug is brought to its place by raising the reservoir, care being taken not to drive it into the narrower portion of the passage. The problem now is to "boil out" the space occupied by the mercury in such a thorough manner that no air will be left between it and the glass, and this is readily accomplished after a little practice. The upper end of the column and the finer tube above are cautiously heated. When the vapor has developed to a certain extent, the whole body of the mercury is driven by the pressure a short distance down the tube. It is immediately brought back and the upper portion of the metal is again heated. After a few repetitions of the procedure, the end of the tube is closed. While closing, it is necessary to have the air in the manometer under somewhat diminished pressure in order that the softened glass may collapse, and the mercury is again driven a short distance down the tube; but on cooling it reascends and fills completely the space in the upper end of the manometer and, ordinarily, no difficulty is thereafter experienced in consequence of its dislodgement or the breaking of the column. The column of mercury in the closed end of the manometer is made considerably longer than would be necessary if only the form of the tube in this region were in doubt. It is made to fill, likewise, all that portion of the tube, lower down, whose caliber may have been altered by heating the glass while closing the instrument.

The manometers which were used in the earlier work were provided with one bulb, which was located on the descending limb of the instrument. The arrangement, however, led to frequent disasters while closing the cells, due to the considerable oscillations of the mercury column during the rather violent manipulation which is necessary for the proper insertion of the manometer stoppers. The air, on such occasions, often escaped from the ascending calibrated limb into the descending one, making necessary an opening and refilling of the instru-

ment. Attention has already been called to this difficulty and the proposed remedy, namely, the blowing of a second bulb near the bottom of the ascending limb. Our present manometers, therefore, have two bulbs, and the one which was more recently introduced serves not only to prevent escape of air while the cell is being closed, but also as a storage place for the air while the operation of closing the manometer in the manner described above is in progress.

A further improvement in manometers, which has served to reduce materially the earlier experimental difficulties, concerns the form of the permanently open end of the instrument, *i. e.*, the end which is submerged in the solution in the cell. The crowding upwards of the manometer under the pressure of the contents of the cell has, from the first, been one of the most persistent of the many troubles which had to be met in the attempt to reduce the measurement of osmotic pressure to a reasonably accurate quantitative basis. The slipping of the manometer in the stopper is attended by a dilution of the solution in the cell, the exact magnitude of which it is impossible to ascertain. If the displacement were limited to the manometer, the extent of the dilution could be quite accurately computed, but it never is so restricted. The material of the rubber stopper is likewise displaced to a greater or smaller extent whenever the manometer is pushed upwards. The exact extent of the upward movement of the manometer is known in every case from the record of the observations taken at the telescope, but it cannot be ascertained how much of this is due to slipping and how much to lack of rigidity in the stopper. Consequently, no entirely safe correction is available for the increase in the capacity of the cell. Hence the endeavor has been, from the beginning, to fix the manometer in the stopper so tightly, and to render the rubber about it so rigid, that the former cannot slip and the latter cannot "bulge." The arrangements which had been made with this end in view were already quite elaborate when the first series of formal measurements of the pressure of cane sugar solutions was undertaken, and they were fully described in the account of that

work. A number of useful changes have, however, since been made which will be explained.

Formerly, a bulb was blown near the open end of the manometer, the idea being that any upward movement of the instrument while in the cell would be quickly arrested through the rapidly increasing resistance of the material of the stopper. The enlargement of the end of the tube has been found indispensable; but the blowing of a bulb in this position produced a cavity which is always necessarily filled with the solution under investigation, and which must, therefore, be emptied and cleansed after each experiment and refilled before the succeeding one. The diameter of the passage into the bulb is, however, only about 0.5 mm., and the withdrawal or introduction of liquids through it by means of fine pipettes is slow and troublesome. Hence the bulb has been replaced by an enlargement of the tube, which is made without increasing its bore, and any solution which is within the manometer can now be expelled by simply inclining the instrument until the mercury appears at the open end. The introduction of liquid is equally easy since, for this purpose, it is only necessary to incline the manometer as before and then, after submerging the open end, to return it to the vertical position.

The enlargement on the manometer does not alone suffice to prevent slipping in the stopper except in the case of quite dilute solutions. If no further precautions are taken, the manometer usually rises until the upper third or half of the enlargement is within the lower end of the stopper, giving rise to a dilution of the solution of unknown and undeterminable magnitude. To prevent this we proceed as follows: Several hours before a manometer is to be used, the stopper, after it has been softened to the right degree (between the teeth, and *not with a caustic alkali*), is cemented with a rubber solution to the tube just above the enlargement. It is then tightly tied near the lower end with a single turn of waxed shoemaker's thread. The lower portions of the rubber are thus crowded downwards and made to expand slightly and cover a small part of the upper portion of the enlargement. If the operation has been rightly performed, the enlargement does not

afterwards ascend any farther into the stopper, however great the pressure in the cell.

After closing the cell, the portion of the stopper which remains outside, *i. e.*, above the glass tube, must be made as rigid as possible. Formerly, we sought to do this by tightly winding the upper end of the stopper with strips of insulating tape; but the support thus given to the sides was not always sufficient, and the tape winding has accordingly been discarded for one of waxed shoemaker's thread, which is much more effective.

Another modification of former practice which may properly be mentioned in this connection, concerns the glass tubes which are inserted in the cells for the reception of the manometers. We have had no trouble with the bursting of the clay cells made by ourselves in the laboratory, not one of them having yet cracked under pressure. The glass tubes, on the other hand, have very frequently cracked, not only while under pressure, but perhaps quite as often, and without any apparent cause, while the cells were not in use. When repeatedly subjected to pressure, the glass which we have hitherto employed becomes quite unreliable. To what extent its unfortunate conduct is due to original defects, we are, of course, unable to determine. Great care has always been exercised in the selection of the tubes, and each one has been subjected to all practicable tests before using it; we are, nevertheless, prepared for the breaking of any one of them while closing the cell, or while under pressure, or even while the cell is lying idle. Both the Bohemian and the Jena tubing have been tried with unsatisfactory results, and finally we have resorted to a lead glass which, it is hoped, will prove more durable.

The method of calibrating the manometer has already been fully described,¹ and we have found no reason for making any essential change in that procedure. But certain corrections, which were neglected in the earlier work, are now applied to the measurements of the volume of the air, and these will be mentioned.

When a manometer has been filled and the volume of the

¹ THIS JOURNAL, 34, 6.

enclosed air is determined for the first time, both ends of the mercury column are located in tubes of equal caliber; but when a measurement is made, the case is different. One end of the column is then in the narrow tube, and the other in the much more capacious bulb on the descending limb of the manometer. Accordingly, a correction for capillary depression is in order, and this is now applied to all readings. The magnitude of the correction is determined experimentally for each instrument, and not calculated from the known caliber of the manometer.

A further correction, which is of some importance in the case of concentrated solutions, is for *meniscus*. Under present conditions the air in the manometer is imprisoned between two mercury columns, and the error resulting from the double meniscus is appreciable when the volume of the air to be measured is small. The diameter of the bore of each manometer is, therefore, determined with a view to eliminating this source of error. The form of the meniscus is assumed, according to the custom in such cases, to be strictly spherical.

Possible corrections, which we have not yet applied, are for the deviations in the conduct of air, under pressure, from the laws of Boyle and of Gay-Lussac. But since the deviations are in each case small, even under our highest pressures, and since the errors resulting from them are of a mutually compensating character, they may with propriety be neglected until some other sources of error, of greater effect upon the results, have been brought under better control. The same may be said of a correction for the distension of the cell under the pressure of its contents. The cell is undoubtedly somewhat expanded during the measurement of pressure, and the solution is therefore somewhat more dilute than it is assumed to be. But dilution due to a distension of the cell under pressure is probably small as compared with that from another cause, which will be mentioned. When a cell is filled with a solution for a measurement of pressure, the porous wall is full of water and some time elapses before the cell can be effectively closed. In the meantime the solution within is rapidly diluting itself by sucking in water from without. We have not

yet been able to devise any means of preventing this dilution of the solution, and must still content ourselves with an endeavor to keep it within bounds by manipulating with the greatest rapidity which is consistent with the safety of the cell and the manometer.

An improvement in our cathetometer, which we devised for the purpose of facilitating final adjustments of the telescope and for determining the distance of any point on the scale from the line above or below it, *i. e.*, for reading the fractions of a millimeter, will perhaps have an interest for others. The usual arrangement for final adjustment on cathetometers of the type of ours tilts the telescope to one side. The design of the elevating device in these instruments is such that the pressure is applied only on one side of the sliding collar upon which the telescope is mounted, whereas it should be applied on all sides equally. If, therefore, the collar is in the smallest degree imperfectly fitted to the rod along which it glides, side-wise displacements are bound to occur. The simple device shown in Fig. VIII. not only remedies this difficulty, but it provides at the same time a satisfactory substitute for the micrometer eye-piece of the telescope.

The upper and heavier end of the set collar *a* has cut upon it a thread of 1 mm. pitch, over which runs the internally threaded, milled and graduated collar *b*. The whole weight of the telescope and its balanced carriage rests upon *b* at *c*, and is uniformly distributed. Upon *e*, but not seen in the figure, is a zero line and, on either side of this, a vernier scale. The raising and lowering of the telescope in the final adjustment is effected by turning *b* to the right or left, and without any tilting or sidewise displacement of the instrument. Considered as a substitute for the micrometer eye-piece, the arrangement has several advantages. In the first place there is no "back-lash" in the threaded parts because the pressure is always upon the same side of the thread, whether the telescope is moving upwards or downwards. Secondly, it is not necessary to have the standard scale located at some fixed distance from the telescope. In other words, the correctness of the readings is not dependent on the distance of the object, hence the de-

vice may be used for measurements upon objects at different distances, *e. g.*, upon the standard scale, and a manometer which is nearer or more distant than the scale. Finally, it is more correct in principle than the micrometer eye-piece, since all the various lines of vision are parallel to each other.

Some change has been made in the process for the removal of air from the porous walls of the cells previous to the deposition of the membranes. It is still removed by means of electrical endosmose, but the texture of the cells is so dense that water passes through the walls very slowly—probably not one-tenth as fast as through the walls of the best cells which were made for us by the potters. This great density of texture was found to be an indispensable characteristic of good cells, and without it we have never been able to obtain maximum pressures. But with increasing closeness of texture in the cell wall came diminishing endosmose, and we were, therefore, impelled to search for an electrolyte which should give a more rapid endosmose than the potassium sulphate which we had previously employed. Accordingly, a series of quantitative comparisons was made by one of us (Frazer) of salts having a common anion, with a view to ascertaining which of the cations would, under our conditions, carry the water through the cell wall most rapidly. Lithium was found to be far more efficient in this respect than potassium or any other metal of the alkalis or alkaline earths. Hence we now employ lithium sulphate for the expulsion of air.

The results of the work mentioned above appear to suggest the existence of a definite relation between the velocity of migration of ions and endosmose. The slower the cation the larger the endosmose has been found to be, and the general rule which is deducible from the measurements at hand is the following: *The quantities of water carried through the porous wall, under identical conditions, are inversely proportional to the relative velocities of the various cations divided by their respective valencies.* All of the results conform, within 3 per cent, to this rule, and the subject has been thought worthy of the more extensive and careful investigation which is now in progress in this laboratory.

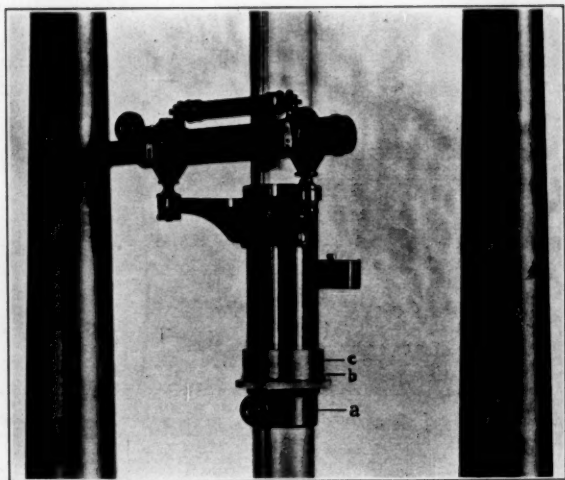


Fig. VIII.

Some of the observations which we have made regarding membranes may be of assistance to others who are working in the same line, and we shall venture to formulate briefly those which have been frequently verified and have proved useful to us, though in doing so we shall run the risk of repeating some facts which have been stated elsewhere.

1. The resistance of a membrane appears to depend principally upon the porosity of the cell in which it is deposited. The finer the pores of the cell the higher will be the maximum resistance of the membrane. It follows that each cell should be found to have a maximum membrane resistance which is characteristic of itself, and this is true, within certain limits, of all the cells with which we have worked. The cells differ greatly among themselves in this respect. For example, the maximum obtainable resistance in one may be between 30,000 and 40,000 ohms, in another between 90,000 and 100,000 ohms, and in a third perhaps over 300,000 ohms. If the membrane in a given case fails to reach approximately the maximum resistance which is characteristic of its cell, it is known that some trouble exists, and that no reliable measurements will be obtained by setting the cell up with a solution. The nature of the trouble is always obscure, but the remedy which is usually effective consists in soaking the cell for several hours in distilled water. On repeating the membrane-forming process, a higher resistance is invariably obtained, but it may be necessary to repeat the soaking several times before the maximum is reached.

2. The pressure rises more rapidly at first in a cell whose membrane resistance is low, *i. e.*, in a quite porous cell than in one in which the membrane has a high resistance, but the maximum pressure of a solution is developed in a shorter time in the latter than in the former. In general, it may be said that the higher the resistance of the membrane, the shorter will be the time required for the development of maximum pressure. For example, a solution may develop its highest pressure within 3 hours in a cell with a resistance of 300,000 ohms, but not within 24 hours in one in which the resistance is 100,000 ohms.

3. The concentration of a solution appears to have no relation whatever to the time required for the development of maximum pressure. With a given cell a normal and a one-tenth normal solution of the same substance require nearly the same time, provided the resistances of the membranes are about equal in the two cases.

4. Solutions of different substances reach their highest pressures in different times. A solution of glucose, for instance, is much slower in reaching its maximum pressure than is one of cane sugar. It appears probable, though we cannot yet affirm it positively, that, in general, substances of large molecular weight develop their highest pressures more quickly than those of small molecular weight.

5. The first membrane which is deposited in a cell will rarely give with any solution the highest pressure which is known to be normal to it, and it may give only a small fraction of it. Hence it is necessary in all cases to build up a membrane by degrees. The procedure which we have found best adapted to this purpose is the following: The new cell is subjected to the membrane-forming process until the resistance becomes stationary and has continued so for some time, or until it exhibits a tendency to decline. The cell is then soaked for several hours in water, and the first treatment is repeated. The membrane may, on the second trial, exhibit the same maximum as before, but it is probable, if the construction of the cell is mechanically perfect, that the resistance will go higher. But, whatever the result on the second trial, the procedure is repeated in all its details again and again until it is certain that the resistance can be forced no higher by further repetitions, and until it is thought that a sufficient body of the membrane has been deposited. Since the current is exceedingly small, a very long time is required for the precipitation of enough of the copper ferrocyanide to cover adequately the whole interior of the cell, and one is liable to a miscalculation as to the readiness of the cell for the next stage of its development.

The highest *habitual* resistance which is developed by the first course of treatment may not be, and usually is not, the

same as that which afterwards comes to be recognized as the characteristic maximum resistance of the cell. A *packing* and *mending* process is still necessary in order to prepare the membrane for use, and until this is completed one cannot hope to obtain reliable measurements of pressure. It appears that, notwithstanding the high resistance of the membrane at the close of the first stage of its development, it is still not so tightly pressed against the cell wall that it cannot be ruptured by pressure. The second process is, therefore, one of rupturing the membrane, wherever possible, by pressure, of crowding it more tightly against the cell wall by the same means, and of mending simultaneously the rents which have been produced. The cell is set up with a fairly concentrated solution of cane sugar—usually 0.5 weight normal—to which has been added a certain amount of potassium ferrocyanide; and to the water in which the cell is immersed there is added an equivalent amount of copper sulphate. One might expect, in view of the fact that the material which is employed in mending the rents is deposited under pressure and, therefore, close to the wall, that the solution would in time develop its normal maximum pressure, but it rarely does so. The pressure rises, often with considerable rapidity, to a maximum which may be maintained for a long time, but this highest pressure is usually considerably below what the normal maximum for the solution is known to be. When it is found that no higher pressure is developed by longer standing, the cell is taken down, emptied, rinsed, soaked in water which is frequently renewed, and then it is again subjected to the membrane-forming process. A higher resistance than the previous maximum will probably be obtained. If so, the cell is again set up with a solution of cane sugar containing potassium ferrocyanide, etc. If, on the other hand, the membrane exhibits a lower, or no higher, resistance than it did before the cell was set up with the sugar solution, the cell is repeatedly soaked in water and resubjected to the membrane-forming process until no further improvement in the resistance of the membrane can be effected, when it is again set up with a solution of sugar. This process of bursting the membrane and of mending the rents, alternately under pres-

sure and by means of the current, is continued until it reaches an habitual maximum of resistance beyond which it cannot be forced, and until the cell gives, within a reasonable time, what are known to be normal maximum pressures with solutions of cane sugar.

We have described our method of preparing a cell in considerable detail because we know from long experience and from many failures that no reliable measurements of osmotic pressure can be obtained with a membrane which has been prepared with less care, or which has been less-thoroughly tested. The pains we take with our membranes is certainly the minimum which will give any validity to the results, and, in our judgment, speculation based upon measurements with membranes which have been less carefully tested as to their efficiency is utterly futile.

6. It may properly be asked what assurance we have that the highest pressures which we obtain are really the *true* maximum pressures of the solutions; whether, in other words, it is not possible that, with still better membranes, even higher pressures would be obtained. We have had this question constantly before us, and have tried to answer it in the only possible way, that is, by trying continually, in every way known to us, to improve the membranes. The result is that we obtain always the *same* maximum of pressure for a given concentration of cane sugar solution, despite our efforts to produce a membrane which will give a still higher pressure.

The question of *leakage* by the membrane is involved with that of maximum pressures, and it has not been neglected. It has, in fact, been tested in every practicable way—by careful examination of the liquid in which the cell was immersed during the development of pressure, and by determination of the concentration of the cell contents afterwards, and our experience in this direction may be summed up as follows: Membranes may be prepared, in the manner described above, which are wholly impermeable to cane sugar up to weight-normal concentration of solution. If prepared with less care, they usually leak, and the failure of many membranes to give the highest pressures is due to leakage. A solution in a cell with

6

a leaking membrane may exhibit a nearly constant pressure for a long time, thus giving one who has had but little experience with membranes the impression that he is observing the true maximum pressure of the solution. The difficulty of preparing non-permeable membranes increases as the molecular weights of the substances diminish. A membrane which is non-permeable to cane sugar may, for instance, leak glucose. It is still possible to obtain satisfactory measurements of osmotic pressure by a differential method, even though the membrane is not wholly non-permeable to the substance in solution. If the leakage is slight, we find that the pressures rise to a highest value and remain constant for a considerable time; and that the same result is reached, time after time, with a given concentration of solution, showing that in such cases an equilibrium of conditions is established, under which, it is to be supposed, the solution is exerting its maximum pressure. If so, and the concentrations of the solutions both within and without the cell can be determined, we may obtain all the data which are necessary for a correct interpretation.

The leakage of membranes can be considerably diminished, and in some instances entirely stopped, through the coöperation of the membrane-forming salts. It was stated¹ in the account given of the first series of measurements of the osmotic pressure of cane sugar solutions that we always added to the solution a small amount of potassium ferrocyanide, and to the water on the outside of the cell, a small equivalent quantity of copper sulphate. This practice has been continued. The quantities of the salts so used (and which are still used) were, per 100 grams of water, 8.46 milligrams of the ferrocyanide and 12.48 milligrams of copper sulphate. It was assumed that these quantities of the salts are osmotically equivalent and that, being on opposite sides of the membrane, the pressures of the solutions in the cells would not be affected by their presence. The assumption was, however, based on the supposition that potassium ferrocyanide dissociates in dilute solutions into five ions, whereas the recent work of Jones and Bassett² on the depression of the freezing points of solutions of this salt make it

¹ THIS JOURNAL, 34, 31.

² *Ibid.*, 34, 311.

appear probable that the dissociation is into *eight* ions instead of *five*, as formerly supposed. If this is true, there may have been a slight excess of pressure in our cells, due to a lack of osmotic equality between the quantities of ferrocyanide and sulphate which were used, and it may, therefore, be necessary to apply a small correction when the exact magnitude of the discrepancy has been ascertained.

The use of the membrane-forming salts in the manner indicated is of great service in the measurement of pressure, and it appears probable that the efficiency of few membranes could be long maintained without their coöperation. It appears probable, moreover, that it will be desirable, and perhaps necessary in some instances, to employ them in larger quantities than hitherto in cases where it is otherwise difficult or impossible to prepare a membrane sufficiently non-permeable to the substance in solution. Accordingly, we have undertaken to ascertain for ourselves the state of dissociation and the actual osmotic inequalities of the two salts, not only in the quantities we desire to use, but also, as nearly as possible, under the same experimental conditions. The results already obtained indicate that a very small correction is to be applied for an overpressure on the part of the ferrocyanide when the quantities and the relative proportions of the membrane-forming salts are such as we have hitherto employed.

Soon after beginning the measurement of the osmotic pressure of glucose solutions, there appeared upon one of our cells an abundant growth of a fungus, which, upon examination, was found to be *penicillium*. Within a few days it appeared upon one after another of the remaining cells until all were affected in the same manner as the first. We then exposed several solutions of glucose to the air of the laboratory, and the fungus appeared in all of them in a short time. We had had no similar experience previously, though we had worked with solutions containing invert sugar for more than two years, and the conditions under which we were working were, in general, unfavorable to the fungus. The sudden prevalence of *penicillium* spores in the atmosphere of the laboratory could, however, be accounted for, though it had not been anticipated.

At the time, certain changes were in progress in a lower part of the building which involved the tearing away of old walls, and the atmosphere of all parts of the laboratory was, in consequence, in a somewhat dusty condition.

It could not be doubted that the same growth extended over the interior walls of the cells, and that its development there would be attended by chemical changes in the glucose whose effect upon the pressures of the solutions could not be ascertained or estimated. The situation was rendered still more difficult to deal with by certain facts which have been frequently verified and have often given us trouble. All of our experience has been to the effect that anything which acts chemically upon the membrane, even in a slight degree, or which tends to modify its physical condition, destroys its efficiency; and that when a membrane has once been injured in either of these ways, it is difficult, and in the majority of cases impossible, to restore it to a sound condition.

It was clear then that some poison for the *penicillium* must be found which would fulfil the following conditions: (1) It must be effective in such small quantities that the pressure of the solutions would not be sensibly effected by its presence; (2) it must not act chemically or otherwise upon the membrane; and (3) it must have no chemical action upon the glucose. It was desirable, moreover, that the substance should be one which would, at the same time, prevent ordinary alcoholic fermentation, though it had been found that this could be avoided by other suitable means.

We were, therefore, greatly restricted in the choice of agents for the destruction of *penicillium* with which the cells had become infected, and for the prevention of its development in the solutions of glucose. Everything of an alkaline or of a distinctly acid character was excluded from the outset, and the information which was accessible to us regarding the action of other possible agents was exceedingly meager and indefinite. Poisons of the phenol type appeared most likely to serve the purpose, but no specific information could be obtained as to their efficacy in the case of *penicillium*. Therefore a series of simple experiments was undertaken with phenol, salicylic

acid and thymol, and to this list of substances were added hydrocyanic acid and chloroform. Some experiments were also made with potassium cyanide, though no assistance could be expected from this compound, because of its alkaline character and its action upon other cyanides.

All the test solutions were made 0.5 weight normal with respect to glucose, and they were freely exposed to the air while under observation. During the daytime they were maintained at a temperature of 30°, and at night they were placed where the temperature did not fall much below 20°.

1. *Salicylic Acid*.—Two solutions of glucose, one of which contained salicylic acid in the proportion of 5.5 grams per 1,000 liters, were exposed. The presence of *penicillium* became apparent in the pure sugar solution on the fourth day, and in the solution containing the salicylic acid, on the seventh day.

The experiment was repeated with double the amount of salicylic acid—i. e., 11 grams per 1,000 liters—in one of the solutions. The fungus appeared in the solution containing only glucose on the third day, and in that containing salicylic acid on the sixth day.

It was clear that salicylic acid, in the concentration employed, could at best only retard the development of *penicillium*. Nevertheless, it was decided to ascertain whether the acid is injurious to the membrane. Accordingly, a cell, which had previously conducted itself in a satisfactory manner, was set up with a 0.5 N solution of glucose containing 11 grams of salicylic acid per 1,000 liters. It failed to develop the full normal pressure, and on the third day the mercury in the manometer began to fall. It was therefore concluded that the salicylic acid had probably attacked the membrane.

2. *Phenol*.—A 0.5 N solution of glucose was made 0.001 N with respect to phenol. The *penicillium* appeared on the seventh day and grew rapidly thereafter. Other similar experiments were tried with similar results, and it was concluded that phenol in very dilute solutions is but little, if any, more poisonous to *penicillium* than is salicylic acid.

6

3. *Thymol*.—The usual solution of glucose was made 0.001 N with respect to thymol. It remained perfectly clear for 11 days. On the twelfth day it became slightly cloudy. But as the solution had in the meantime nearly lost the characteristic odor of thymol, the experiment was inconclusive. A vigorous growth of the fungus which had developed in a glucose-phenol solution was therefore removed to a fresh one of glucose and thymol. It soon began to diminish in size and continued to shrink until the eighth day, when it was examined under the microscope and found to be apparently dead. But that it was still living was shown by its subsequent revival, after 2 days, in a sterilized Pasteur's solution. Further experiments with thymol showed conclusively that minute quantities of it suffice not only to prevent the development of *penicillium* in glucose solutions, but also, in time, to kill the living fungus, and it remained for us to ascertain whether its presence is without injurious effect upon the membrane. The first experiments along this line were indecisive. An infected cell was soaked for 4 days in a 0.001 N solution of thymol and then subjected to the membrane-forming process. The resistance of the membrane rose quickly to 33,000 ohms, which was its usual and normal value in the cell in question. Such behavior is ordinarily regarded as evidence of the sound condition of a membrane, but on setting the cell up with a glucose solution containing the usual proportion of thymol, it failed to develop more than 60 per cent of the normal pressure. The conduct of the cell on the first trial, however, was probably due to injury to the membrane during the growth of the *penicillium*, for later, after numerous repetitions of the process heretofore described for the improvement of membranes, it was finally restored to a condition in which it gave normal pressures with glucose solutions containing the usual amount of thymol.

4. *Hydrocyanic Acid*.—A vessel containing a solution of glucose in which a large quantity of *penicillium* was growing vigorously was placed under a bell jar beside another vessel containing potassium cyanide, and into the latter acid was dropped from a funnel. After several hours the fungus was

examined under the microscope. It appeared to be dead, and it did not revive when placed in Pasteur's solution.

A cell infected with *penicillium*, which, before its infection, had given normal pressures with cane sugar solutions, and whose normal resistance was about 75,000 ohms, was filled with water and suspended under a bell jar in an atmosphere of hydrocyanic acid gas. After 12 hours it was removed, cleansed, and subjected to the membrane-forming process. In 20 minutes the resistance rose to 40,000 ohms, but immediately thereafter it began to decline, and at the end of 80 minutes its resistance was only 22,000 ohms. On repeating the treatment, after a thorough soaking in water, the resistance rose to 40,000 ohms in 15 minutes. It then began to decline, as on the previous occasion. The cell was nevertheless set up with a 0.5 weight-normal solution of glucose, which was 0.001 N with respect to thymol. The pressure rose to 11 atmospheres and continued undiminished for 3 days. The conduct of this cell during the first stage of restoration is described because it is unusual for a cell, behaving as it did, to give a pressure so near to correct maximum. Its subsequent conduct was not remarkable, since it required ten repetitions of the usual treatment to restore the membrane to sound condition.

5. *Potassium Cyanide*.—Notwithstanding the impossibility of employing potassium cyanide for our purpose, owing to its destructive action upon the membranes, it was of some interest to compare its efficacy as a poison with that of hydrocyanic acid and thymol. A 0.5 N solution of glucose was made 0.001 N with potassium cyanide and exposed in the usual way. On the eighth day the *penicillium* appeared. As the cyanide had probably all disappeared within that time, owing to chemical transformations, a fresh glucose-cyanide solution was prepared, and into it was introduced a vigorous mass of the *penicillium*. The growth of the fungus appeared to be checked for a time, but on microscopic examination the second day, it was found to be living, and on the third day it was again growing vigorously.

6. *Chloroform*.—Solutions containing *penicillium* were exposed to vapors of chloroform and also treated with small

quantities of it in liquid form, but no marked poisonous effects could be observed.

Of all the substances tested, thymol appeared to be the one best suited to our purpose. It was found to be sufficiently poisonous to *penicillium* when used in quantities so minute that the pressures of the solutions are not sensibly affected by its presence; and what is of equal importance, its presence in small quantities appeared to have no deleterious effects upon the membranes. It is also satisfactory as a preventive of ordinary alcoholic fermentation, which must be carefully guarded against in working with solutions of glucose.

It is probable that hydrocyanic acid could also be employed for our purposes, but since its use is attended with great inconvenience, and thymol answers all our requirements, we have not thought it necessary to experiment any further along that line.

An account of the formal measurement of the osmotic pressure of glucose solutions will be given in Part II. of this paper.

JOHNS HOPKINS UNIVERSITY,
May 1, 1906.

A REDETERMINATION OF THE OSMOTIC PRESSURE AND OF THE DEPRESSION OF THE FREEZING POINTS OF CANE SUGAR SOLUTIONS.¹

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The conclusion reached by Morse and Frazer¹ regarding the magnitude of the osmotic pressure of cane sugar solutions was expressed in the following words:

"Cane sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state. In other words, dissolved cane sugar exerts an osmotic pressure throughout the larger volume of the solution equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent."

¹ The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution.

² THIS JOURNAL, 34, 93 (1905).

This conclusion was the obvious deduction from the results which were obtained by the measurement of the osmotic pressure of thirteen concentrations of solution ranging from 0.05 to 1.0 gram-molecular weight of sugar dissolved in 1,000 grams of water. The authors believed, moreover, that, after devoting several years to the problem, they had developed the method of measuring osmotic pressure to a point where reliable results were to be expected, and they were inclined, therefore, to assign to them a high degree of trustworthiness, and to regard them as probably sufficient to establish the conclusion with which all of them harmonized in so striking a manner.

There were, however, certain reasons why a redetermination of the osmotic pressure of cane sugar solutions should be undertaken. In the first place, the directly experimental quantitative evidence regarding osmotic pressure, which was previously on record, is meager and wholly inadequate to establish firmly any view whatsoever regarding its magnitude. Hence any measurement of the force which has the virtue of precision is at the present time useful, and cane sugar lends itself to work of this kind more readily and over a wider range of concentrations than any other available substance. It is obtainable in any quantity desired and in a high state of purity, is sufficiently soluble, and, above all, it is practicable to prepare membranes which are wholly impervious to it.

In the second place, the method as employed in the first series of measurements was still susceptible of considerable improvements, which, if introduced, would materially reduce or wholly remove certain known sources of error. Moreover, a number of small corrections had been neglected in the earlier work, which, under the improved experimental conditions, could be appropriately applied. It was reasonable to expect, therefore, that results approximating more closely to the real osmotic pressures of the solutions could be secured by a second series of measurements than had been obtained by the first.

It was stated in the earlier communication¹ that the measurements of the osmotic pressure of cane sugar solutions would be repeated at an early date, and that the sources of error to

¹ THIS JOURNAL, 34, 92 (1905).

which particular attention would be given were three in number: (1) The "thermometer effects," (2) the uncertainty regarding the capacity of the closed end of the manometer, and (3) the inversion which takes place in the cell.

The measures which were taken to eliminate the thermometer effects, and the uncertainty regarding the capacity of the manometer in the region in question, have been fully described in the preceding paper (p. 2) and it need only be said of them here that they were effective.

Regarding the last of the three principal sources of error, namely, the inversion which takes place in the cell, some statements made in the first communication will be recalled:

1. The attempt was made to determine the extent of the inversion by the method of Fehling.¹

2. The inversion which took place in the cells was always greater than that which occurred in portions of the same solutions which were set aside for comparison at the close of the experiments.² This observation has been confirmed in all of our subsequent work, but the cause of it has not yet been ascertained.

3. The opinion was expressed³ that the inversion in the more concentrated solutions was, in reality, greater than it was apparently found to be by the method which was employed to determine it, and it was stated that, when the work was repeated, the polariscope would be used to measure the inversion which takes place in the cell. The suspicion that the amount of inversion had been underestimated in the earlier work, which was aroused by observations that could not be tested at the time, has since been confirmed.

In conformity with our purpose to describe adequately whatever is new in our procedure, we shall now state the essential facts concerning the preparations which were made for the polariscopic work.

The instrument used is the Schmidt and Haensch half-shadow polariscope, with double wedge compensation and

¹ THIS JOURNAL, 34, 31 (1905).

² *Ibid.*, 34, 30 (1905).

³ *Ibid.*, 34, 92 (1905).

triple field of vision. The length of tube which it accommodates is 4 decimeters, and a small incandescent electric lamp is employed for illumination.

As the basis of the system upon which we are working—a gram-molecular weight of substance dissolved in 1,000 grams of water (both corrected for air displacement)—differs widely from that ordinarily employed in saccharimetric work, it was necessary either to recalculate the standard data and find their values in terms of our system, or to construct a table of corrections from data obtained by ourselves. We followed the former course, taking the precaution, however, to verify experimentally several of the computed results. It is not necessary to explain the method of calculation, but we give in full the table of corrections which was computed and has been used in the present work. The values appearing in the table are the weights of invert sugar which, in a 2 decimeter tube, produce a loss of 1° in rotation (at 19°, 20°, 21°, 22° and 23°) in the solutions whose pressures we have measured.

Table I.—*Invert Sugar in Grams per 1,000 Grams of Water, which Produced a Loss of 1° in Rotation.*

Weight-normal concentration.	Temperature.					
	18°.	19°.	20°.	21°.	22°.	23°.
0.10	2.12	2.13	2.14	2.15	2.15	2.16
0.20	2.16	2.17	2.18	2.19	2.20	2.21
0.30	2.21	2.22	2.23	2.23	2.24	2.25
0.40	2.25	2.26	2.27	2.28	2.29	2.30
0.50	2.31	2.32	2.32	2.33	2.34	2.35
0.60	2.34	2.35	2.36	2.37	2.38	2.38
0.70	2.38	2.39	2.40	2.41	2.42	2.43
0.80	2.43	2.44	2.44	2.45	2.46	2.47
0.90	2.47	2.48	2.49	2.50	2.51	2.52
1.00	2.51	2.52	2.53	2.54	2.55	2.56

Since one molecule of cane sugar yields two of invert sugar, the correction for inversion is made by deducting from the observed pressure one-half the calculated pressure of the invert sugar which is found by the polariscope. The loss in rotation may, however, not be due exclusively to inversion. A part of it may result from a *dilution* of the cell contents, and dilution may, in turn, be brought about by an increase in the capacity

of the cell, or by a leaking of the membrane. The last source of error, leakage, is excluded by the pains we have taken in the present work to ascertain that the membranes employed were really impervious to cane sugar. On the other hand, some loss of rotation from dilution, due to an increase in the capacity of the cell, has at times been unavoidable, and it will be seen later on that we have, in a few cases, attempted to discriminate between inversion and dilution as causes of the diminished rotation of the solutions.

All that need be said regarding the preparation and the testing of the membranes has been fully explained in the preceding paper. It may not be superfluous, however, to restate here, in a general way, the more important facts concerning them, namely: (1) That the membranes are prepared for their work by an elaborate and time-consuming course of treatment, involving deposition by the current, followed by a bursting of them by pressure and a mending of the rents, first under pressure and subsequently by the current, until a resistance is reached which can be forced no higher by a continuation of the process; (2) that the membranes are tested as to their permeability by examining the water in which the cells are immersed during an experiment for the presence of the dissolved substance. The results given in this paper were all obtained with membranes which did not leak cane sugar.

The method of calibrating the manometers, which was explained in a former paper,¹ has been adhered to without any essential modification. On the other hand, important changes have been made in the form of the manometer and in the method of closing it and preparing it for insertion in the cell. All of these matters have been discussed in the preceding paper (p. 20), and certain of them will be mentioned again in connection with an account of the corrections which have been applied to the measurements of pressure.

The values given in the present paper are all computed on the basis of *one* for the atomic weight of hydrogen. The theoretical molecular weight of cane sugar is, therefore, 339.6 instead of 342.22, which was the value used in the earlier

¹ THIS JOURNAL, 34, 6 (1905).

paper. Accordingly, the standard weight of the theoretical gas becomes 2 grams instead of 2.02 grams, and its theoretical pressure, under standard conditions of volume (1 liter) and of temperature (0°), at Baltimore is 22.265 atmospheres instead of 22.488 atmospheres. On this basis, the formula for computing molecular weight¹ from osmotic pressure is

$$M = W \frac{22.265 + 0.0817t}{P},$$

in which M is the molecular weight, P the observed osmotic pressure, W the weight of the substance dissolved in 1,000 grams of water, 22.265 the theoretical pressure of a gram-molecular weight of a gas at 0° when its volume is reduced to 1 liter, and 0.0817 is the temperature coefficient, either of gas or of osmotic pressure.

It will hardly be necessary to recall the fact that our solutions are all made by dissolving a gram-molecular weight of the substance, or some decimal part thereof, in 1,000 grams of water, and that both weights are corrected for air displacement. The material used in the present investigation, as in the earlier one, was the purest obtainable "rock candy."

The corrections which have been applied are numerous, and some of them are of considerable importance. All of them have, however, been discussed more or less fully elsewhere, particularly in the preceding paper, and a brief recapitulation will suffice for present purposes, except in the case of the correction for inversion.

1. *The Correction of the Manometer for Inequalities of Bore.*—

The method of calibrating a manometer is explained in the first paper² on the measurement of the osmotic pressure of cane sugar solutions, and, as stated above, we have found no reason for changing in any essential respect the procedure there described. The manometers used in the present work were calibrated with unusual care, and in each case with repetitions of the procedure until all the discordances in the recorded data were well within the limits of reasonable errors of observation.

¹ THIS JOURNAL, 34, 32 (1905).

² *Ibid.*, 34, 6 (1905).

The uncertainty regarding the true volume of the manometer in the region of the closed end was pointed out¹ in the same paper, and the means by which this difficulty and another of analogous character were finally overcome are explained on page 21 of the preceding communication.

In this connection may also be mentioned, as having an indirect bearing on the accuracy of the results, the later improvements² in manometers, consisting in the introduction of a bulb on the ascending limbs and the substitution, for the bulb near the open ends, of a thick spherical mass of glass which is made without increasing the bore of the tube.

2. *The Correction for Capillary Depression.*—As explained on page 26, when the volume of the air in a manometer is determined for the first time, no correction for capillary depression is necessary because both ends of the mercury column which separates the gas in the manometer from the outside air are located in tubes of the same internal diameter. The case is different when a measurement is made. The increasing pressure in the cell drives the mercury column forward until its rear end is within the bulb on the descending limb of the manometer, the diameter of which is many times that of the other end of the column, and a correction for capillary depression is therefore necessary. We have determined experimentally the magnitude of this correction for each of the manometers which was used in the present work, and it has been applied to all the measurements here recorded.

We have been duly mindful throughout of the fact that, in manometric work in narrow tubes, gross errors may result from an impure condition of the mercury, and great care has been taken to prepare the mercury which is used in the manometers in the highest possible state of purity.

3. *The Correction for Meniscus.*—In the form of manometer now used by us, the air is located between two mercury columns, and the correction for meniscus is of considerable importance when the pressure of a concentrated solution is measured. The following example will illustrate this: Under a pressure of 25 atmospheres, approximately that of a weight-

¹ THIS JOURNAL, 34, 10 (1905).

² *Ibid.*, 36, 22 (1906).

normal solution at 25° (not corrected for atmospheric pressure) the length of the air column is reduced to about 18 mm. in one of the manometers, and the correction for the double meniscus is about 0.2 mm., or nearly 0.3 atmosphere. In order to ascertain the magnitude of the correction to be applied for meniscus, the internal diameter of each manometer is determined by the usual micrometric method, and the volume of the meniscus is calculated on the assumption that the end of the mercury column is hemispherical in form when its diameter does not much exceed 0.5 mm.

4. *The Correction for Liquids in the Manometer.*—When a cell is closed and the manometer nut is screwed down upon the stopper for the purpose of fixing the latter firmly in its place and of bringing a suitable initial pressure upon the contents of the cell, the solution enters the manometer, pushing the mercury before it until the surface of contact between the two has receded to some point in the bulb on the descending limb of the manometer. We have thus two liquids in the manometer whose pressure must be ascertained and added as a correction to that which is calculated from the volume of the air, and the magnitude of this correction must be determined in part before the cell is placed in the bath, because afterwards nothing is in sight except that portion of the manometer which contains the air. The virtual height of the solution is the difference in level between the water outside of the cell and the surface of contact between the two liquids in the manometer bulb, and this is determined at once by the cathetometer. The density of the solution is, of course, known. The virtual height of the mercury is the difference in level between the surface of contact in the bulb and the upper end of the column, the position of which is not fixed until the pressure becomes constant. It is, therefore, necessary in this preliminary work to determine the difference in level between the surface of contact of the two liquids in the bulb and some fixed point on the ascending limb of the manometer, which is always in sight. The difference in level between the point of reference and the top of the mercury column can then be ascertained at any time, and the correction for the adverse pressure of mercury com-

pleted. The necessary fixed points of reference are provided for by etching upon the manometer tubes two fine lines, one of which is located near the bottom and the other near the top of the ascending limbs. The assumption is made that when the cell is ready to be placed in the bath no further movement of the surface of contact between the two liquids in the bulb occurs, which is not strictly true. But, inasmuch as the manometer nut is screwed down in all cases until a relatively high initial pressure has been obtained, and the diameter of the bulb is many times that of other parts of the manometer tube, the error resulting from this unavoidable assumption is insignificant.

The presence of a small portion of the solution in the bulb of the manometer, at a considerable distance from the membrane through which water enters the cell, and in the narrow channel connecting this portion with the main body of the solution, could not fail to bring to the front at once a question of importance, namely, the question (to state it in a general way) of the *distribution of the water which passes through the membrane into the solution.*

We can only say that we attacked the problem experimentally more than three years ago and found it an excessively difficult one to solve and that we have not yet enough well established facts to justify any discussion of the subject on our part. Nevertheless, a brief statement of our procedure may not be out of place. We attempted to determine at intervals the concentration of the solution at different distances from the membrane, but were thrown into confusion by the discovery of the fact that water passes through the membrane at different rates in different areas, and that the rate of passage in the different areas depends on the porosity of the wall behind them. As we could produce no cells with perfectly uniform porosity throughout, this line of investigation was abandoned, and we afterwards devoted six months to experimenting upon the effect of stirring the solution on the rate of intake of water, and on the final magnitude of the pressures. Here, again, we were baffled by the complexity of the determining conditions, and the data which we gathered have no present value, though it

is hoped that later they may contribute something toward the solution of the problem. We do not hesitate to express the opinion that any theoretical solution of it will be unsatisfactory, owing to the impossibility of giving due weight to each one of the many conditions which are involved. We have not, up to this time, made any observation which has led us to suspect that we are getting less than maximum pressures because of a failure on the part of the water taken into the cell to distribute itself with sufficient rapidity or sufficiently uniformly through the solution.

5. *The Correction for Loss in Rotation.*—We have stated already that the diminished rotation of the solutions is due to two causes: First, and principally, to the inversion of the cane sugar which occurs in the cell, and secondly, to an increase in the capacity of the cell which is necessarily followed by dilution. Dilution from leakage, as we have already explained, is excluded by the care we have taken to ascertain that no sugar had escaped from the cell. It is not possible in any case to determine exactly how much of the loss in rotation is due, on the one hand, to inversion, and, on the other, to dilution; but it is safe to affirm that, in our experiments, the loss from the second cause is usually so small as compared with that from the first, no great error is committed by ascribing all loss of rotation to inversion. In a few instances, nevertheless, we have attempted, as will be seen later, to assign a certain minimum value to the dilution effect.

Dilution of the cell contents, excluding that due to a possible escape of the dissolved substance, is brought about in various ways, which will be enumerated:

(a) The capacity of the cell is, doubtless, somewhat increased in consequence of a distension of the containing walls under pressure. We have taken no measure up to the present time to ascertain the magnitude of this effect, but it is believed to be small and safely negligible until other sources of error have been brought under better control. We have taken the trouble, however, to assure ourselves occasionally that the length of the manometers is not sensibly increased by the highest possible pressures. The test is easily made by measuring

the distance between the two reference lines on the vertical limbs.

(b) When the cell is filled and closed, a certain "initial" pressure is brought upon the contents by mechanical means, but, as this is always less than the final osmotic pressure of the solution, there is a subsequent rise of the mercury in the manometer, and the space occupied by the solution is increased by an amount exactly equal to the contraction of air in the manometer. The volume of the water which is thus taken into the cell to expand the solution to its new and final limits is known, for we determine not only the inequalities of bore in the manometers, but also the absolute volume of the calibration units. We are, therefore, prepared to calculate at any time the extent of the dilution of the solution from the cause under consideration. If we take into account (1) the fact that the "initial" pressures are the highest which we consider it safe to establish, (2) that the internal diameter of the manometer tubes is very small—ranging between 0.5 and 0.6 mm., and (3) that the capacity of the cell proper is between 18 and 25 cc., it will be seen that the volume of the water taken in is insignificant as compared with the original volume of the solution, and that its effect as a diluent may be neglected.

The knowledge of the absolute volumes of the calibration units is useful in another way. It enables us to ascertain at any time the exact volume of the solution which is within the manometer, and therefore to form a rough estimate of the effect upon pressure if this less fortunately situated portion of the solution should fail to obtain its due share of the water which enters the cell through the membrane.

(c) As mentioned elsewhere, when a cell is filled with a solution some time elapses before it can be closed and the proper amount of "initial" pressure can be brought to bear upon the solution. In the meantime the solution is sucking in water from the wet porous wall, and constantly becoming more dilute. There are no means of wholly preventing this dilution, or of estimating its magnitude. We attempt to keep it down to the lowest limits by inserting the wet cell in a flexible rubber cap, by rinsing the interior of the cell many times

with the solution before filling it, and, finally, by manipulating with the utmost rapidity while closing the cell.

(d) We come now to what, in our judgment, is the largest single source of experimental error in our work, namely, the use of the rubber stopper in closing the cell. We have considered or tried every expedient which suggested itself as giving any promise of enabling us to dispense with it, but have found them all less satisfactory, on the whole, than the stopper itself. The difficulty is due, of course, to the lack of rigidity in the stopper. The means which have been resorted to with a view to keeping the stopper in its place, and to rendering the portion of it which remains outside of the cell so rigid that no internal pressure will suffice to increase the capacity of the cell, by crowding upwards either the manometer itself, or portions of the stopper, or both, have been described in various places in these papers. It must be admitted, however, that these measures have not always been effective, and that some dilution of the cell contents, which is due to the cause in question, usually occurs. In the majority of the measurements the effect is so small that no considerable error is committed by ascribing all loss of rotation to inversion. In the remaining cases, as will be explained, the loss in rotation can be approximately distributed between inversion and dilution.

After placing a cell in the bath, the first thing which is determined is the location of the upper reference line on the manometer. The position of this line should remain stationary throughout the experiment, and it will do so if there is no slipping of the manometer in the stopper, or crowding of the material of the latter out of place, either or both of which necessarily sends the manometer upwards. The exact amount of the upward displacement of the manometer is measured in every instance, and, if it were due solely to slipping in the stopper, the resulting dilution of the solution could be quite accurately calculated. But, as a rule, there is, under present conditions, little slipping of the manometer in the stopper. Most of the upward movement of the manometer during an experiment is due, unfortunately, to a distortion of the stop-

per, the effect of which upon the volume of the cell contents cannot be accurately estimated.

In the following table is given the upward displacement of manometer in each of the experiments recorded in this paper. There are also given the corresponding losses in rotation of the cell contents :

Table II.—Displacement of Manometer and Loss in Rotation.

Weight-normal concentration of solution.	Number of the experiment.	Upward displacement of the manometer: mm.	Loss in rotation in degrees.	Weight-normal concentration of solution.	Number of the experiment.	Upward displacement of the manometer: mm.	Loss in rotation in degrees.
0.1	1	0.07	0.5	0.6	1	3.78	2.8
	2	0.54	0.5		2	0.83	1.9
0.2	1	2.78	0.7	0.7	3	0.64	1.8
	2	1.44	0.7		1	0.24	2.6
	3	0.19	0.5		2	0.07	2.2
0.3	1	0.12	0.5	0.8	1	0.32	3.2
	2	0.10	0.6		2	1.80	3.9
0.4	1	0.30	0.8	0.9	1	1.21	2.5
	2	1.18	1.3		2	0.87	2.4
0.5	1	0.16	1.4	1.0	1	0.88	2.4
	2	0.32	1.2		2	2.97	4.0

The smallest upward displacement of the manometer was less than 0.1 mm (0.08 mm.), while the greatest was 3.78 mm. It will be noticed, moreover, on comparing the different determinations of a given concentration with respect to displacement of manometer and loss in rotation that where the former is large the latter is likewise considerable. For example, in the case of the 0.6 weight-normal solution, of which three measurements of pressure were made, the displacements of the manometer were 0.64 mm. (Expt. 3), 0.83 mm. (Expt. 2), and 3.78 mm. (Expt. 1), and the corresponding losses in rotation were 1°.8, 1°.9 and 2°.0. It is reasonable to suppose that the amount of inversion was not greater in Experiment 1 of this series than in Experiments 2 and 3, and that the greater loss in rotation in that case was due to a greater dilution of the

cell contents. That more dilution did take place in Experiment 1 than in 2 and 3 is proved by the greater displacement of the manometer. This assumption has been made the basis of an attempt to discriminate, in a few instances, between loss of rotation due to inversion and that due to dilution. It is assumed, for example, in the case of the 0.6 N solution, as stated above, that the inversion in Experiment 1 was probably not greater than in Experiments 2 and 3, and, therefore, in correcting for loss of rotation in Experiment 1, 1°.8 of the loss is ascribed to inversion and 1° to dilution. This procedure only partially corrects for the dilution of the cell contents, since all crowding of the manometer out of its place is attended by an increase in the capacity of the cell. Hence, in Experiments 2 and 3, some of the loss in rotation is undoubtedly due to dilution though it is all ascribed to inversion. In presenting the results in the latter part of this paper, two tables of data are given wherever an attempt has been made to distribute the loss in rotation between inversion and dilution. In one of these is given the result as it would be if all loss is ascribed to inversion, and in the other the result as it is found to be on distributing the loss in accordance with the plan explained above.

The ideal substance for the precise determination of osmotic pressure is one which suffers no chemical change in the cell, which does not escape through the membrane, and whose concentration of solution can be accurately determined, preferably by the polariscope. With such a substance, all loss of concentration in the cell would necessarily be due to dilution, and the extent of this could be correctly determined.

In Table III. the data given in Table II. are repeated, and there are added other columns showing (1) the deviations of the results, in fractions of an atmosphere from theoretical gas pressures if all losses of rotation are ascribed to inversion, (2) the distribution of the diminished rotation of the cell contents between inversion and dilution wherever such an apportionment has been made, and (3) the differences between theoretical gas pressures and the results when the latter are corrected for dilution :

Table III.

Weight-normal concentration of solution.	Number of the experiment.	Upward displacement of the manometer. mm.	Loss in rotation in degrees.	Deviation from gas pressure if all loss in rotation is ascribed to inversion. (Atmosphere.)	Loss in rotation due to inversion.	Loss in rotation due to dilution.	Deviation from gas pressure if correction for dilution is made.
0.1	1	0.07	0.5	+0.10	0.5		
	2	0.54	0.5	+0.13	0.5		
0.2	1	2.78	0.7	-0.14	0.5	0.2	-0.07
	2	1.44	0.7	-0.09	0.5	0.2	-0.02
	3	0.19	0.5	0.00	0.5		
0.3	1	0.12	0.5	+0.03	0.5		
	2	0.10	0.6	+0.03	0.6		
0.4	1	0.30	0.8	+0.03	0.8		
	2	1.18	1.3	-0.11	0.8	0.5	+0.06
0.5	1	0.16	1.4	0.00	1.4		
	2	0.32	1.2	+0.12	1.2		
0.6	1	3.78	2.8	-0.18	1.8	1.0	+0.19
	2	0.83	1.9	+0.15	1.9		
	3	0.64	1.8	+0.23	1.8		
0.7	1	0.24	2.6	+0.02	2.6		
	2	0.07	2.2	+0.03	2.2		
0.8	1	0.32	3.2	-0.05	3.2		
	2	1.80	3.9	-0.23	3.2	0.7	+0.03
0.9	1	1.21	2.5	-0.04	2.5		
	2	0.87	2.4	+0.08	2.4		
1.0	1	0.88	2.4	+0.23	2.4		
	2	2.97	4.0		2.4	1.6	-0.23

The results which were obtained by the measurement of the osmotic pressure of ten concentrations of solutions—ranging from 0.1 to 1.0 gram-molecular weight of sugar dissolved in 1,000 grams of water, are given in the following tables. All of the determinations, with the exception of three, were made in a single cell—that which, according to our system of designation, is called G. The last three determinations were made with A and B, the cells with which we began the measurement of the osmotic pressure of cane sugar. The reappearance of A and B on the work, owing to the cracking of the glass tube in

G, is noteworthy as an indication of the durability of good cells. A and B have been in more or less continuous use for over a year, and were withdrawn from service in the measurement of the pressure of glucose solutions for the completion of the present work.

Every cell has what may be called its idiosyncrasies of behavior. G is noteworthy, among other things, for its high resistance, and for the rapidity with which solutions in it reach a maximum pressure.

Tables IV. to XXX., inclusive, contain, in an abridged form, the record of the individual determinations of pressure. The actual readings by the telescope have been omitted owing to the great space which they occupy. Otherwise the record is purposely made so complete that one can not only follow the development of pressure in every case, but also recalculate the results.

In Tables XXXI. and XXXII. much of the data contained in Tables IV. to XXX. has been brought together under the titles "Summary of Conditions" and "Summary of Results," and some comment upon these tabulations is called for.

1. Table XXXI. *Summary of Conditions.* It will be noticed (column 3) that three different cells, G, A and B, were used in the present work. G is a new cell and has not been employed for other measurements of pressure. It is noteworthy for the high resistance of its membrane, which ranges (column 4) between 372,000 and 158,550 ohms, with a usual value of about 270,000 ohms. The former value is the highest which it has been possible to obtain by repetitions of the course of treatment which has been explained elsewhere. The other resistances given in the table were likewise *maxima* in the sense that they could not be forced any higher without interrupting the current, soaking the cell in water, etc. The minimum, 158,550 ohms, is the lowest resistance with which we have thought it safe to set up the cell for a formal measurement.

A and B are old cells which have been in service nearly continuously for over a year. They are, in fact, the first wholly satisfactory cells which were produced in the laboratory, after

Table IV.

Original wt. normal concentration of solution, 0.1. Experiment No. 1.
 Rotation of original solution, $12^{\circ}.8$ ($t = 20^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $12^{\circ}.3$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, $0^{\circ}.5$. Resistance of membrane, 350,000 ohms.
 Calibration units of air in manometer, 402.13. Initial pressure, 2.10 atmospheres.
 Time of setting up cell, 1.00 P. M., April 7, 1906.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer, etc.	Inversion.	Capillary depression.							
April 7.															
6.00 P. M.	24°.00	24°.00	144.46												
7.45 "	24°.00	24°.07	144.12	132.43	1.00	0.51	0.07	0.02	2.50	2.41	+0.09	329.09			
April 8.															
12.00 A. M.	24°.05	23°.80	143.64	132.17	1.00	0.51	0.07	0.02	2.50	2.41	+0.09	329.14			
10.00 "	24°.10	23°.70	142.81	131.38	1.00	0.51	0.07	0.02	2.52	2.42	+0.10	326.58			
2.30 P. M.	24°.10	23°.50	142.72	131.39	1.00	0.51	0.07	0.02	2.52	2.42	+0.11	326.58	327.85		

Upward displacement of manometer = 0.07 mm.

Table V.

Original wt. normal concentration of solution, 0.1. Experiment No. 2.
 Rotation of original solution, $12^{\circ}.8$ ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $12^{\circ}.3$
 ($t = 19^{\circ}$).
 Capillary depression, 0.02 atmosphere.
 Cell used, G.

Loss in rotation, $0^{\circ}.5$.
 Resistance of membrane, 275,000 ohms.
 Calibration units of air in manometer, 402.13.
 Initial pressure, 2.20 atmospheres.
 Time of setting up cell, 5.00 P. M., April 9, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Difference between pressure found and calculated.	Theoretical gas pressure, corrected.	Osmotic pressure, corrected.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer, etc.	Inversion.	Capillary depression.						
April 9.														
8.00 P. M.	24° 15	24° 10	144.56											
April 10.														
12.00 A. M.	24° 20	24° 10	142.45	130.88	0.99	0.51	0.07	0.02	2.53	2.42	+0.11	325.40		
8.30 "	24° 20	23° 90	141.31	129.92	0.99	0.51	0.07	0.02	2.56	2.42	+0.14	321.58		
11.00 "	24° 25	24° 00	141.36	129.91	0.99	0.51	0.07	0.02	2.56	2.43	+0.13	321.63		322.56
12.30 P. M.	24° 25	24° 10	141.32	129.84	0.99	0.51	0.07	0.02	2.56	2.43	+0.13	321.63		

Upward displacement of manometer = 0.54 mm.

Upward displacement of manometer = 0.54 mm.

Table VI.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
 Rotation of original solution, 25° ($t = 20^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of experiment, $24^{\circ}.3$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, $0^{\circ}.7$. Resistance of membrane, 271,250 ohms.
 Calibration units of air in manometer, 461.34. Initial pressure, 1.98 atmospheres.
 Time of setting up cell, 12.30 P. M., March 3, 1906.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer, etc.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.				
March 3.															
5.50 P. M.	20° 00	21° 64		144.08											
11.00 "	20° 20	22° 00		96.69											
March 4.															
12.00 M.	20° 65	21° 84		95.67	88.57	0.99	0.52	0.10	0.02	4.66	4.79	-0.13	349.10		
7.00 P. M.	20° 85	21° 90		95.71	88.59	0.99	0.52	0.10	0.02	4.66	4.79	-0.13	348.53		
11.30 "	20° 95	21° 94		95.83	88.69	1.00	0.52	0.10	0.02	4.64	4.79	-0.15	350.97		
March 5.															
10.20 A. M.	21° 15	21° 99		95.85	88.69	1.00	0.52	0.10	0.02	4.64	4.80	-0.16	351.21		

See Table VII. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 2.78 mm.

Table VII.

Time.	Solution.	Temperature.	Volume of air in manometer.		Corrected.	Atmospheric pressure.	Liquids in manometer.	Corrections.		Osmotic pressure, corrected.	Theoretical R. a. s. pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
			Uncorrected.	Corrected.				Loss in rotation.	Capillary depression.					
March 3.														
5.50 P. M.	20° 00	21° 64	144.08											
11.00 "	20° 20	22° 00	96.69											
March 4.														
12.00 M.	20° 65	21° 84	95.67	88.57	0.99	0.52			0.02	4.73	4.79	-0.06	343.93	
7.00 P. M.	20° 85	21° 90	95.71	88.59	0.99	0.52			0.02	4.73	4.79	-0.06	344.16	
11.30 "	20° 95	21° 94	95.83	88.69	1.00	0.52			0.02	4.71	4.79	-0.08	345.76	344.96
March 5.														
10.20 A. M.	21° 15	21° 99	95.85	88.69	1.00	0.52			0.02	4.71	4.80	-0.09	345.99	

Due to inversion = -0.07.
 Due to dilution = +0.04.

Original wt. normal concentration of solution, 0.2.
 Experiment No. 1.
 Rotation of original solution, 25° ($t = 20^\circ$).
 Rotation at conclusion of experiment, 24° 3 ($t = 20^\circ$).
 Loss in rotation, 0° 7.
 Calibration units of air in manometer, 461.34.
 Time of setting up cell, 12.30 P. M., March 3, 1906.

Resistance of membrane, 271,250 ohms.
 Initial pressure, 1.98 atmospheres.

Manometer used, No. 4.
 Capillary depression, 0.02 atmosphere.
 Cell used, G.

See Table VI.
 Upward displacement of manometer = 2.78 mm.

Table VIII.

Original wt. normal concentration of solution, 0.2.
 Rotation of original solution, 25° ($t = 20^{\circ}$).
 Rotation at conclusion of experiment, $24^{\circ}.3$
 ($t = 20^{\circ}$).
 Loss in rotation, $0^{\circ}.7$.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 4.30 P. M., March 6, 1906.

Time.	Solution.	Temperature.	Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.	
			Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.					
March 6.														
9.10 P. M.	20° 90	22° 04	110.41											
March 7.														
10.30 A. M.	21° 20	22° 19	83.05	76.79	1.00	0.58	0.10	0.02	4.74	4.80	-0.06	343.86		
2.20 P. M.	21° 30	22° 25	83.14	76.89	1.00	0.58	0.10	0.02	4.73	4.80	-0.07	344.70		
4.40 "	21° 30	21° 64	83.18	77.06	1.00	0.58	0.10	0.02	4.72	4.80	-0.08	345.43		
9.00 "	21° 35	21° 54	83.62	77.49	1.00	0.58	0.10	0.02	4.69	4.80	-0.11	347.70		
March 8.														
10.15 A. M.	21° 73	22° 74	84.09	77.61	0.99	0.58	0.10	0.02	4.69	4.80	-0.11	348.14		

See Table IX. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 1.44 mm.

Table IX.

Original wt. normal concentration of solution, 0.2. Experiment No. 2.
 Rotation of original solution, 25° ($t = 20^\circ$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 24° 3' Capillary depression, 0.02 atmosphere.
 ($t = 20^\circ$). Cell used, G.

Loss in rotation 0° 7'. Resistance of membrane, 280,000 ohms.
 Calibration units of air in manometer, 402.13. Initial pressure, 2.30 atmospheres.
 Time of setting up cell, 4.30 p. m., March 6, 1906.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Mean molecular weight.		
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.		Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.
March 6.	9.10 P. M.	20° 90	22° 04	110.41								
March 7.	10.30 A. M.	21° 20	22° 19	83.05	76.79	1.00	0.58	0.02	4.81	4.80	+0.01	338.85
	2.30 P. M.	21° 30	22° 25	83.14	76.89	1.00	0.58	0.02	4.80	4.80	0.00	339.67
	4.40 "	21° 30	21° 64	83.18	77.06	1.00	0.58	0.02	4.79	4.80	-0.01	340.38
	9.00 "	21° 35	21° 54	83.62	77.49	1.00	0.58	0.02	4.76	4.80	-0.04	342.58
March 8.	10.15 A. M.	21° 73	22° 74	84.09	77.61	0.99	0.58	0.02	4.76	4.80	-0.04	343.02

See Table VIII.

Upward displacement of manometer = 1.44 mm.

Table X.

Original wt. normal concentration of solution, 0.2. Experiment No. 3.
 Rotation of original solution, $24^{\circ}.9$ ($t = 20^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, $24^{\circ}.4$ Capillary depression, 0.02 atmosphere.
 ($t = 20^{\circ}$). Cell used, G.
 Loss in rotation, 0.5. Resistance of membrane, 225,400 ohms.
 Calibration units of air in manometer, 402.13. Initial pressure, 2.13 atmospheres.
 Time of setting up cell, 4.50 P. M., March 8, 1906.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
				Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.		
March 8.													
8.30 P. M.		$21^{\circ}.50$	$22^{\circ}.44$	86.15									
March 9.													
12.45 A. M.		$21^{\circ}.65$	$22^{\circ}.64$	83.00	76.63	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.37
8.30 "		$21^{\circ}.80$	$22^{\circ}.69$	83.02	76.64	0.98	0.59	0.07	0.02	4.81	4.81	0.00	339.54
10.30 "		$21^{\circ}.85$	$22^{\circ}.74$	83.15	76.74	0.98	0.59	0.07	0.02	4.80	4.81	-0.01	340.31

Upward displacement of manometer = 0.19 mm.

Table XI.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
 Rotation of original solution, $36^\circ.5$ ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 36° ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $0^\circ.5$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 275,000 ohms.
 Time of setting up cell, 4.00 P. M., March 14, 1906. Initial pressure, 3.50 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.						Molecular weight calculated from osmotic pressure.	Mean molecular weight.
				Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	
March 14.													
8.15 P. M.	$21^\circ.55$	$22^\circ.10$		56.91									
11.50 "	$21^\circ.60$	$22^\circ.30$		56.65	52.37	1.00	0.62	0.07	0.02	7.25	7.21	+0.04	337.68
March 15.													
10.45 A. M.	$21^\circ.70$	$22^\circ.04$		56.80	52.55	0.99	0.62	0.07	0.02	7.23	7.21	+0.02	338.72
3.00 P. M.	$21^\circ.70$	$22^\circ.24$		56.84	52.55	0.99	0.62	0.07	0.02	7.23	7.21	+0.02	338.72

Upward displacement of manometer = 0.12 mm.

Table XII.

Time.	Temperature.			Volume of air in manometer.			Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.						
March 17.															
5.00 P. M.	19°.65	21°.75	56.88												
9.00 "	19°.70	22°.20	56.75	52.47	1.01	0.62	0.08	0.02	7.21	7.16	+0.05	337.36			
March 18.															
12.00 A. M.	19°.85	22°.34	56.80	52.50	1.01	0.62	0.08	0.02	7.21	7.16	+0.05	337.53			
11.15 "	20°.10	21°.34	56.85	52.72	1.02	0.62	0.08	0.02	7.17	7.17	0.00	339.70			338.2

Upward displacement of manometer = 0.10 mm.

Original wt. normal concentration of solution, 0.3. Experiment No. 2.
 Rotation of original solution, 36°.6 ($t = 15^\circ$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 36° ($t = 15^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 0°.6. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 273,250 ohms.
 Time of setting up cell, 1.00 P. M., March 17, 1906. Initial pressure, 3.40 atmospheres.

Table XIII.

Original wt. normal concentration of solution, 0.4. Experiment No. 1.
 Rotation of original solution, $48^{\circ}.1$ ($t = 16^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of expt., $47^{\circ}.3$ ($t = 16^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $0^{\circ}.8$. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 372,300 ohms.
 Time of setting up cell, 12.00 M., March 10, 1906. Initial pressure, 6.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Air in manometer.		Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
March 10.													
6.00 P. M.	$21^{\circ}.45$	$21^{\circ}.84$	49.41										
8.30 "	$21^{\circ}.48$	$22^{\circ}.20$	49.19	45.48	1.00	0.58	0.12	0.02	9.62	9.61	+0.01	339.17	
March 11.													
2.00 A. M.	$21^{\circ}.60$	$22^{\circ}.39$	49.15	45.42	1.00	0.58	0.12	0.02	9.64	9.61	+0.03	338.61	338.73
11.00 "	$21^{\circ}.70$	$22^{\circ}.54$	49.15	45.40	1.00	0.58	0.12	0.02	9.64	9.61	+0.03	338.72	
12.30 P. M.	$21^{\circ}.75$	$22^{\circ}.59$	49.14	45.39	1.00	0.58	0.12	0.02	9.65	9.61	+0.04	338.43	

Upward displacement of manometer = 0.30 mm.

Table XIV.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
 Rotation of original solution, 48° ($t = 17^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $46^\circ.7$ ($t = 17^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^\circ.3$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 277,500 ohms.
 Time of setting up cell, 5.15 P. M., March 12, 1906. Initial pressure, 4.30 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
				Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.		
March 12.													
8.00 P. M.	22°.00	22°.	44	47.31									
March 13.													
12.00 A. M.	22°.10	22°.	59	43.27	39.96	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.47
10.00 "	22°.15	22°.	44	43.29	40.00	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.52
12.30 P. M.	22°.20	22°.	60	43.29	39.98	1.01	0.64	0.19	0.02	9.52	9.63	-0.11	343.58

See Table XV. for distribution of loss in rotation between inversion and dilution.

Upward displacement of manometer = 1.18 mm.

Table XV.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
 Rotation of original solution, 48° ($t = 17^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $46^\circ.7$ ($t = 17^\circ$). Capillary depression, 0.02 atmospheres.
 Loss in rotation, $1^\circ.3$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 277,500 ohms.
 Time of setting up cell, 5.15 P. M., March 12, 1906. Initial pressure, 4.30 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrected.	Uncorrected.	Corrections.					Mean molecular weight.	
	Solution.	Air in manometer.	Atmospheric pressure.	Liquids in manometer, etc.			Loss in rotation.	Due to inversion = -0.12.	Due to dilution = +0.10.	Capillary depression.	Osmotic pressure, corrected.		Theoretical gas pressure.
March 12.	8.00 P. M.	22° .00	22° .44	47.31									
March 13.	12.00 A. M.	22° .10	22° .59	43.27	39.96	1.01	0.64		0.02	9.69	9.63	+0.06	337.44
	"	12.15	22° .44	43.29	40.00	1.01	0.64		0.02	9.69	9.63	+0.06	337.50
	10.00 "	22° .15	22° .44	43.29	39.98	1.01	0.64		0.02	9.69	9.63	+0.06	337.55
	12.30 P. M.	22° .20	22° .60	43.29	39.98	1.01	0.64		0.02	9.69	9.63	+0.06	337.55

Table XVI.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
 Rotation of original solution, 59° ($t = 20^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., 57.6 ($t = 20^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^\circ.4$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 274,500 ohms.
 Time of setting up cell, 4.30 p. m., March 19, 1906. Initial pressure, 10.80 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.							Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.			
March 19.														
8.30 P. M.	$22^{\circ}.60$	$22^{\circ}.80$	34.61											
11.30 "	$22^{\circ}.65$	$22^{\circ}.50$	34.55	31.92	0.98	0.65	0.22	0.02	12.07	12.06	+0.01	339.26		
March 20.														
8.00 A. M.	$22^{\circ}.50$	$22^{\circ}.50$	34.55	31.92	0.99	0.65	0.22	0.02	12.06	12.05	+0.01	339.36	339.59	
11.30 "	$22^{\circ}.70$	$22^{\circ}.60$	34.62	31.97	0.99	0.65	0.22	0.02	12.04	12.06	-0.02	340.16		

Upward displacement of manometer = 0.16 mm.

Table XVII.

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
 Rotation of original solution, $58^{\circ}.9$ ($t = 18^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of expt., $57^{\circ}.7$ ($t = 18^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^{\circ}.2$. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 158,550 ohms.
 Time of setting up cell, 4.30 P. M., March 23, 1906. Initial pressure, 4.30 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
				Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
March 23.														
8.15 P. M.		$23^{\circ}.70$	$24^{\circ}.70$	39.67										
March 24.														
12.00 A.		$23^{\circ}.70$	$24^{\circ}.10$	39.29	36.10	1.02	0.60	0.19	0.02	12.19	12.10	+0.09	337.11	
9.15 "		$23^{\circ}.70$	$23^{\circ}.70$	39.10	35.97	1.02	0.60	0.19	0.02	12.25	12.10	+0.15	335.46	
12.00 M.		$23^{\circ}.70$	$23^{\circ}.90$	39.14	35.98	1.02	0.60	0.19	0.02	12.23	12.10	+0.13	336.01	336.19

Upward displacement of manometer = 0.32 mm.

Table XVIII.

Original wt. normal concentration of solution, 0.6 Experiment No. 1.
 Rotation of original solution, $69^{\circ}.2$ ($t = 20^{\circ}$). Manometer used, No. 5.
 Rotation at conclusion of expt., $66^{\circ}.4$ ($t = 20^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^{\circ}.8$. Cell used, G.
 Calibration units of air in manometer, 442.18. Resistance of membrane, 218,000 ohms.
 Time of setting up cell, 5.00 P. M., April 10, 1906. Initial pressure, 11.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical R as pressure, corrected.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.		
April 10.	7.45 P. M.	$24^{\circ}.30$	$24^{\circ}.40$	$24^{\circ}.40$	31.86	29.24	1.00	0.64	0.45	0.02	14.33	14.55	—0.22
April 11.	12.00 A. M.	$24^{\circ}.30$	$24^{\circ}.40$	$24^{\circ}.40$	31.86	29.24	1.00	0.64	0.45	0.02	14.33	14.55	—0.22
	8.30 "	$24^{\circ}.40$	$24^{\circ}.10$	$24^{\circ}.10$	31.74	29.16	1.00	0.64	0.45	0.02	14.37	14.55	—0.18
	11.00 "	$24^{\circ}.40$	$24^{\circ}.20$	$24^{\circ}.20$	31.71	29.12	1.00	0.64	0.45	0.02	14.39	14.55	—0.16
	2.30 P. M.	$24^{\circ}.40$	$23^{\circ}.90$	$23^{\circ}.90$	31.68	29.13	1.00	0.64	0.45	0.02	14.39	14.55	—0.16

See Table XIX. for distribution of loss in rotation between inversion and dilution.
 Upward displacement of manometer = 3.78 mm.

Table XIX.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
Rotation of original solution, $69^{\circ}.2$ ($t = 20^{\circ}$). Manometer used, No. 5.
Rotation at conclusion of expt., $66^{\circ}.4$ ($t = 20^{\circ}$). Capillary depression, 0.02 atmosphere.
Loss in rotation, $2^{\circ}.8$. Cell used, G.
Calibration units of air in manometer, 442.18. Resistance of membrane, 218,000 ohms.
Time of setting up cell, 5.00 p. m., April 10, 1906. Initial pressure, 11.80 atmospheres.

Time.	Solution.		Air in manometer.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
			Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.						
April 10.	24° 30'	24° 40'	34.46												
7.45 P. M.															
April 11.	24° 30'	24° 40'	31.86	29.24	1.00	0.64	Due to inversion = +0.21.	0.02	14.70	14.55	+0.15	336.14			
12.00 A. M.	24° 30'	24° 40'	31.74	29.16	1.00	0.64	Due to dilution = +0.21.	0.02	14.74	14.55	+0.19	335.35			
8.30 "	24° 40'	24° 20'	31.71	29.12	1.00	0.64		0.02	14.76	14.55	+0.21	334.89			335.32
11.00 "	24° 40'	23° 50'	31.68	29.13	1.00	0.64		0.02	14.76	14.55	+0.21	334.89			
2.30 P. M.	24° 40'	23° 50'	31.68	29.13	1.00	0.64		0.02	14.76	14.55	+0.21	334.89			

See Table XVIII.

Upward displacement of manometer = 3.78 mm.

Table XX.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
 Rotation of original solution, $69^{\circ}.2$ ($t = 20^{\circ}$). Manometer used, No. 5.
 Rotation at conclusion of expt., $67^{\circ}.3$ ($t = 20^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^{\circ}.9$. Cell used, G.
 Calibration units of air in manometer, 442 18. Resistance of membrane, 215,000 ohms.
 Time of setting up cell, 5.00 P. M., April 12, 1906. Initial pressure, 10.45 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.					
April 12.	8.00 P. M.	24° 15'	24° 50'	31.60									
April 13.		24° 15'	24° 30'	31.39	38.82	1.01	0.64	0.30	0.02	14.69	+0.15	336.20	
	12.00 A. M.	24° 20'	24° 40'	31.39	28.81	1.01	0.64	0.30	0.02	14.70	+0.15	336.03	
	9.00 "	24° 20'	24° 40'	31.39	28.80	1.01	0.64	0.30	0.02	14.71	+0.16	335.90	336.07
	1.00 P. M.	24° 30'	24° 55'	31.39	28.81	1.01	0.64	0.30	0.02	14.70	+0.15	336.13	
	2.45 "	24° 30'	24° 80'	31.43	28.81	1.01	0.64	0.30	0.02	14.70	+0.15	336.13	

Upward displacement of manometer = 0.83 mm.

Table XXI.

Original wt. normal concentration of solution, 0.6. Experiment No. 3.
 Rotation of original solution, $69^{\circ}.2$ ($t = 19^{\circ}$).
 Rotations at conclusion of expt., $67^{\circ}.4$ ($t = 19^{\circ}$).
 Loss in rotation, $1^{\circ}.8$.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 12.30 P. M., April 14, 1906.
 Resistance of membrane, 272,500 ohms.
 Initial pressure, 9.00 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.						Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.					
April 14.															
4.30 P. M.	$24^{\circ}.10$	$23^{\circ}.90$	28.79												
7.45 "	$24^{\circ}.10$	$24^{\circ}.00$	28.63												
11.00 "	$24^{\circ}.10$	$24^{\circ}.15$	28.54	26.21	0.99	0.66	0.29	0.02	14.74	14.54	+0.20	335.00			
April 15.															
10.00 A. M.	$24^{\circ}.10$	$24^{\circ}.00$	28.47	26.16	0.99	0.66	0.29	0.02	14.77	14.54	+0.23	334.32			
12.30 P. M.	$24^{\circ}.10$	$23^{\circ}.75$	28.40	26.12	0.99	0.66	0.29	0.02	14.79	14.54	+0.25	333.87			
3.00 "	$24^{\circ}.10$	$23^{\circ}.70$	28.41	26.14	0.99	0.66	0.29	0.02	14.78	14.54	+0.24	334.10			
5.30 "	$24^{\circ}.10$	$23^{\circ}.70$	28.43	26.15	1.00	0.66	0.29	0.02	14.77	14.54	+0.24	334.32			

Upward displacement of manometer = 0.64 mm.

Table XXII.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
 Rotation of original solution, $79^{\circ}.1$ ($t = 22^{\circ}$). Manometer used, No. 4.
 Rotation at conclusion of expt., $76^{\circ}.5$ ($t = 22^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^{\circ}.6$. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 222,000 ohms.
 Time of setting up cell, 5.00 P. M., March 26, 1906. Initial pressure, 9.63 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.						Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
						Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.					
March 26.															
8.15 P. M.		$23^{\circ}.35$	$23^{\circ}.60$	Uncorrected.	Corrected.										
March 27.															
12.00 A. M.		$23^{\circ}.35$	$23^{\circ}.45$	28.16	25.93	1.00	0.61	0.43	0.02	16.99	16.92	+0.07	338.39		
8.30 "		$23^{\circ}.35$	$23^{\circ}.40$	28.25	26.02	0.99	0.61	0.43	0.02	16.94	16.92	+0.02	339.39		
12.00 M.		$23^{\circ}.85$	$23^{\circ}.85$	28.27	26.00	0.99	0.61	0.43	0.02	16.96	16.95	+0.01	339.40		
2.30 P. M.		$24^{\circ}.00$	$24^{\circ}.00$	28.34	26.05	0.99	0.61	0.43	0.02	16.92	16.96	-0.04	340.37		339.39

Upward displacement of manometer = 0.24 mm.

Table XXIII.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
 Rotation of original solution, $79^{\circ}.2$ ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., 77° ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^{\circ}.2$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 280,000 ohms.
 Time of setting up cell, 4.30 P. M., March 30, 1906. Initial pressure, 9.49 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.							Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.		
March 30. 8.30 P. M.	23° .74	23° .80	24.80	22.81	0.98	0.67	0.36	0.02	16.98	16.89	+0.09	338.87	
March 31. 12.00 A. M.	23° .74	24° .00	24.85	22.84	0.98	0.67	0.36	0.02	16.96	16.89	+0.07	339.27	
9.00 "	23° .80	24° .00	24.84	22.83	0.98	0.67	0.36	0.02	16.97	16.95	+0.02	339.14	339.50
12.30 P. M.	24° .30	23° .90	24.94	22.89	0.98	0.67	0.36	0.02	16.92	16.98	-0.06	340.70	

Upward displacement of manometer = 0.07 mm.

Table XXIV.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
 Rotation of original solution, 89° ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $85^\circ.8$ ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $3^\circ.2$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 272,500 ohms.
 Time of setting up cell, 4.15 P. M., April 2, 1906. Initial pressure, 12.70 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Air in manometer.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
April 2.														
8.30 P. M.	$23^\circ.57$	$24^\circ.30$		21.74	19.96	1.01	0.67	0.53	0.02	19.30	19.35	-0.05	340.53	
11.45 "	$23^\circ.60$	$24^\circ.10$		21.76	19.99	1.01	0.67	0.53	0.02	19.26	19.35	-0.09	341.27	
April 3.														
8.30 A. M.	$23^\circ.60$	$23^\circ.60$		21.70	19.97	1.01	0.67	0.53	0.02	19.29	19.35	-0.06	340.73	340.48
12.30 P. M.	$23^\circ.60$	$23^\circ.80$		21.67	19.93	1.01	0.67	0.53	0.02	19.33	19.35	-0.02	340.03	
2.30 "	$23^\circ.60$	$24^\circ.00$		21.67	19.92	1.01	0.67	0.53	0.02	19.34	19.35	-0.01	339.85	

Upward displacement of manometer = 0.32 mm.

Table XXV.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
 Rotation of original solution, 89° ($t = 19^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $85^\circ.1$ ($t = 19^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $3^\circ.9$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 223,000 ohms.
 Time of setting up cell, 4.30 P. M., April 16, 1906. Initial pressure, 15.10 atmospheres.

Time.	Temperature.		Air in manometer.		Corrected.		Corrections.						Theoretical gas pressure.	Osmotic pressure, corrected.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.									
April 16.																	
8.00 P. M.	23° 60	23° 50	22.93														
11.50 "	23° 65	23° 85	21.94														
April 17.																	
9.00 A. M.	23° 70	23° 50	21.78	20.05	1.01	0.67	0.64	0.02	19.09	19.36	—0.27	344.42					
12.30 P. M.	23° 70	23° 30	21.81	20.09	1.01	0.67	0.64	0.02	19.05	19.36	—0.31	345.14					
2.30 "	23° 70	23° 30	21.69	19.98	1.01	0.67	0.64	0.02	19.17	19.36	—0.19	342.98					
5.00 "	23° 70	23° 20	21.67	19.97	1.01	0.67	0.64	0.02	19.18	19.36	—0.18	342.80					
8.00 "	23° 65	23° 10	21.68	19.99	1.01	0.67	0.64	0.02	19.16	19.36	—0.20	343.10					

See Table XXVI. for distribution of loss in rotation between inversion and dilution.

Upward displacement of manometer = 1.8 mm.

Table XXVI.

Original wt. normal concentration of solution, 0.8.
 Rotation of original solution, 89° ($t = 19^\circ$).
 Rotation at conclusion of expt., 85.1° ($t = 19^\circ$).
 Loss in rotation, $3^\circ.9$.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 4.30 P. M., April 16, 1906.
 Resistance of membrane, 223,000 ohms.
 Initial pressure, 15.10 atmospheres.

Time.	Solution.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between calculated and pressure found.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
				Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	etc.	Loss in rotation.	Capillary depression.				
April 16.														
8.00 P. M.	$23^\circ.60$	$23^\circ.50$		22.93										
11.50 "	$23^\circ.65$	$23^\circ.85$		21.94										
April 17.														
9.00 A. M.	$23^\circ.70$	$23^\circ.50$		21.78	20.05	1.01	0.67			0.02	19.35	-0.01	339.79	
12.30 P. M.	$23^\circ.70$	$23^\circ.30$		21.81	20.09	1.01	0.67			0.02	19.31	-0.05	340.49	
2.30 "	$23^\circ.70$	$23^\circ.30$		21.69	19.98	1.01	0.67			0.02	19.43	+0.07	338.39	339.08
5.00 "	$23^\circ.70$	$23^\circ.20$		21.67	19.97	1.01	0.67			0.02	19.44	+0.08	338.22	
8.00 "	$23^\circ.65$	$23^\circ.10$		21.68	19.99	1.01	0.67			0.02	19.42	+0.06	338.51	

See Table XXV.

Upward displacement of manometer = 1.8 mm.

Table XXVII.

Original wt. normal concentration of solution, 0.9.
 Rotation of original solution, 98° ($t = 22^{\circ}$).
 Rotation at conclusion of expt., $95^{\circ}.5$ ($t = 22^{\circ}$).
 Loss in rotation, $2^{\circ}.5$.
 Calibration units of air in manometer, 442.18.
 Time of setting up cell, 1.00 P. M., May 1, 1906.

Experiment No. 1.
 Manometer used, No. 5.

Capillary depression, 0.02 atmosphere.
 Cell used, A.

Resistance of membrane, 64, 100 ohms.
 Initial pressure, 10.40 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer, etc.	Inversion.	Capillary depression.						
May 1.	8.00 P. M.	24°.00	24°.50	28.27										
May 2.	10.30 A. M.	24°.00	24°.20	22.03										
May 3.	6.30 P. M.	24°.20	25°.15	21.87										
May 3.	10.00 A. M.	24°.65	25°.30	21.53	19.70	0.99	0.66	0.43	0.02	21.71	21.85	-0.14	341.81	
May 3.	1.00 P. M.	24°.70	25°.30	21.50	19.67	0.99	0.66	0.43	0.02	21.73	21.85	-0.12	341.55	
May 3.	5.30 "	24°.80	25°.30	21.43	19.61	0.99	0.66	0.43	0.02	21.81	21.86	-0.05	340.41	
May 3.	11.00 "	24°.90	25°.35	21.35	19.37	0.99	0.66	6.43	0.02	21.90	21.87	+0.03	339.12	340.19
May 4.	10.30 A. M.	24°.90	24°.50	21.22	19.32	0.99	0.66	0.43	0.02	21.97	21.87	+0.10	338.04	

Upward displacement of manometer = 1.21 mm.

Upward displacement of manometer = 1.21 mm.

Table XXVIII.

Original wt. normal concentration of solution, 0.9. Experiment No. 2.
 Rotation of original solution, 98° ($t = 22^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., $95^\circ.6$ ($t = 22^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $2^\circ.4$. Cell used, B.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 84,000 ohms.
 Time of setting up cell, 12.30 P. M., May 1, 1906. Initial pressure, 14.00 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.							Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.		
May 1.													
8.00 P. M.	24° 00	24° 50	21.36										
May 2.													
10.30 A. M.	24° 00	24° 20	19.71										
6.30 P. M.	24° 20	25° 15	19.61										
May 3.													
10.00 A. M.	24° 65	25° 30	19.45	17.82	0.99	0.67	0.41	0.02	21.86	21.85	+0.01	339.47	
1.00 P. M.	24° 70	25° 30	19.48	17.80	0.99	0.67	0.41	0.02	21.88	21.85	+0.03	339.21	
5.30 "	24° 80	25° 30	19.42	17.77	0.99	0.67	0.41	0.02	21.92	21.86	+0.06	338.70	338.82
11.00 "	24° 90	25° 35	19.37	17.72	0.99	0.67	0.41	0.02	21.98	21.87	+0.11	337.89	

Upward displacement of manometer = 0.87 mm.

Table XXIX.

Original wt. normal concentration of solution, 1.0.
 Experiment No. 1.
 Rotation of original solution, $107^{\circ}.2$ ($t = 22^{\circ}$).
 Manometer used, No. 6.
 Rotation at conclusion of expt., $104^{\circ}.8$ ($t = 22^{\circ}$).
 Capillary depression, 0.02 atmosphere.
 Cell used, B.
 Loss in rotation, $2^{\circ}.4$.
 Resistance of membrane, 99,100 ohms.
 Calibration units of air in manometer, 402.13.
 Time of setting up cell, 1.00 P. M., April 27, 1906.
 Initial pressure, 14.60 atmospheres.

Time.	Temperature.		Air in manometer.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.		Uncorrected.		Corrected.		Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.				
April 28. 7.30 P. M.	23° 40'	24° 70'	18.40												
April 29. 12.00 A. M.	23° 50'	24° 75'	17.69												
9.30 "	23° 60'	23° 20'	17.41		16.04	1.00	1.00	0.67	0.41	0.02	24.34	24.19	+0.15	337.63	
1.00 P. M.	23° 55'	23° 30'	17.38		16.01	1.00	1.00	0.67	0.41	0.02	24.40	24.19	+0.21	336.66	
7.00 "	23° 55'	23° 30'	17.37		16.00	1.00	1.00	0.67	0.41	0.02	24.41	24.19	+0.22	336.52	336.39
April 30. 12.00 A. M.	23° 55'	23° 30'	17.33		15.97	1.00	1.00	0.67	0.41	0.02	24.47	24.19	+0.28	335.70	
9.00 "	23° 57'	23° 93'	17.35		15.95	1.00	1.00	0.67	0.41	0.02	24.49	24.19	+0.30	335.45	

Upward displacement of manometer = 0.88 mm.

Table XXX.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.
 Rotation of original solution, $107^{\circ}.4$ ($t = 18^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of expt., $103^{\circ}.4$ ($t = 18^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 4° . Cell used, B.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 84,000 ohms.
 Time of setting up cell, 3.00 P. M., May 7, 1906. Initial pressure, 17.00 atmospheres.

Time.	Solution.	Air in manometer.		Corrected.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
		Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Loss in rotation.	Capillary depression.	Osmotic pressure, corrected.						
May 8.														
12.00 A. M.	24° 90	24° 50	21.05											
10.30 "	24° 70	23° 40	20.50											
7.30 P. M.	24° 60	23° 90	18.15											
11.30 "	24° 60	24° 50	18.17											
May 9.														
10.15 A. M.	24° 60	24° 14	18.07	16.60	1.00	0.67			0.02	23.88	24.28	-0.40	345.22	342.72
2.00 P. M.	24° 60	24° 20	18.00	16.53	1.00	0.67			0.02	23.94	24.28	-0.34	344.35	
6.00 "	24° 60	24° 20	18.01	16.54	1.00	0.67			0.02	23.96	24.28	-0.32	344.07	
May 10.														
12.00 A. M.	24° 60	24° 10	17.94	16.48	1.00	0.67			0.02	24.05	24.28	-0.23	342.78	342.66
9.00 "	24° 50	23° 90	17.93	16.49	1.00	0.67			0.02	24.05	24.28	-0.22	342.66	
Upward displacement of manometer = 2.97 mm.														

Upward displacement of manometer = 2.97 mm.

Due to inversion = 1.41 .
 Due to dilution = 37 .

Table XXXI.—Summary of Conditions.

Weight-normal concentration.	No. of experiment.	Cell used.	Resistance.	Initial pressure. Atmospheres.	Length of time in reaching maximum pressure. Hours.	Length of time cell remained in bath. Hours.	Change of temperature of bath during the experiment. $^{\circ}$ F.	Time over which the temperature extended. Hours.
0.1	1	G	350,000	2.10	7.00	23.00	0 $^{\circ}$.10	14.0
	2	"	275,000	2.20	7.00	19.50	0 $^{\circ}$.05	11.0
0.2	1	"	271,250	1.98	11.00	33.80	0 $^{\circ}$.50	22.0
	2	"	280,000	2.30	18.00(?)	41.75	0 $^{\circ}$.54	24.0
	3	"	225,000	2.13	8.00	17.75	0 $^{\circ}$.20	10.0
0.3	1	"	275,000	3.50	7.75	23.50	0 $^{\circ}$.10	11.0
	2	"	273,250	3.40	8.00	22.25	0 $^{\circ}$.40	14.0
0.4	1	"	372,300	6.80	8.50	24.50	0 $^{\circ}$.27	16.0
	2	"	277,500	4.30	6.75	19.25	0 $^{\circ}$.10	12.0
0.5	1	"	274,500	10.80	7.00	19.00	0 $^{\circ}$.20	3.5
	2	"	158,550	4.30	7.50	19.50	0 $^{\circ}$.00	
0.6	1	"	218,000	11.80	7.00	21.50	0 $^{\circ}$.10	14.0
	2	"	215,000	10.45	7.00	21.75	0 $^{\circ}$.15	15.0
	3	"	272,500	9.00	10.50	17.00	0 $^{\circ}$.00	
0.7	1	"	222,000	9.63	7.00	21.50	0 $^{\circ}$.65	26.0
	2	"	280,000	9.49	4.00	20.00	0 $^{\circ}$.56	12.0
0.8	1	"	272,500	12.00	4.25	22.25	0 $^{\circ}$.03	3.0
	2	"	223,000	15.10	16.50(?)	27.50	0 $^{\circ}$.05	3.0
0.9	1	A	64,100	10.40	45.00(1)	79.50	0 $^{\circ}$.25	13.0
	2	B	84,000	14.00	45.50(1)	58.50	0 $^{\circ}$.25	13.0
1.0	1	"	99,100	14.60	44.50(1)	68.00	0 $^{\circ}$.05	3.5
	2	"	84,000	17.00	43.20(1)	66.00	0 $^{\circ}$.10	9.0
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

Tabl: XXXII.—Summary of Results.

Weight-normal concentration.	No. of experiment.	Maximum and minimum temperatures of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature.	Maximum and minimum differences between osmotic and gas pressures.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24° 0	2.51	2.42	+0.09, +0.11	327.85	
	2	24° .2	2.55	2.43	+0.11, +0.14	322.56	325.21
0.2	1	20° .65	4.72	4.79	-0.06, -0.09	344.96	
	2	21° .2	4.78	4.80	+0.01, -0.04	340.90	
	3	21° .65	4.81	4.81	0.00, -0.01	339.74	341.87
0.3	1	21° .6	7.24	7.21	+0.02, +0.04	338.37	
	2	19° .7	7.20	7.16	0.00, +0.05	338.20	338.29
0.4	1	21° .48	9.64	9.61	+0.01, +0.04	338.73	
	2	22° .1	9.69	9.63	+0.06, +0.06	337.50	338.12
0.5	1	22° .5	12.06	12.06	+0.01, -0.02	339.59	
	2	23° .7	12.22	12.10	+0.09, +0.15	336.19	337.89
0.6	1	24° .3	14.74	14.55	+0.15, +0.21	335.32	
	2	24° .15	14.70	14.55	+0.15, +0.16	336.07	
	3	24° .1	14.77	14.54	+0.20, +0.25	334.32	335.24
0.7	1	23° .35	16.95	16.94	-0.04, +0.07	339.59	
	2	23° .75	16.96	16.93	+0.02, +0.09	339.50	339.55
0.8	1	23° .57	19.30	19.35	-0.01, -0.09	340.48	
	2	23° .65	19.39	19.36	-0.05, +0.07	339.08	339.78
0.9	1	24° .65	21.82	21.86	-0.14, +0.10	340.19	
	2	24° .65	21.91	21.86	+0.01, +0.11	338.82	339.51
1.0	1	23° .55	24.42	24.19	+0.15, +0.30	336.39	
	2	24° .5	24.05	24.28	-0.22, -0.23	342.72	339.56 ⁽⁸⁾

(1) Theoretical molecular weight of cane sugar = 339.60.

Mean molecular weight of cane sugar calculated from the observed osmotic pressure of all concentrations = 337.59.

the conclusion was reached that the potters were not likely to solve the problem of cell-making. A, though still serviceable, has deteriorated in the course of time in respect to the maximum resistance of its membrane, which, in the beginning, was usually over 100,000 ohms. B, on the other hand, now exhibits a higher resistance than formerly.

The conduct of the three cells, G, A and B, with respect to the time required for the development of maximum pressure (see column 6, Table XXXI.), is also noteworthy. In G the solutions usually developed their maximum pressures within 7 hours, while in A and B over 40 hours were required for the same purpose. Both A and B have deteriorated in this respect. In general, it may be said that the interval between the time of setting up A or B and that of the first reading which is made the basis of a calculation of pressure, is now nearly twice as long as formerly. It appears, from the figures in column 6, that in G the solutions differed greatly in regard to the time consumed in reaching the highest pressures. In this respect the figures are somewhat misleading. They really give the time which elapsed between the placing of the cell in the bath and the taking of the first reading *after* an approximately maximum pressure had been reached, and in several instances the first formal reading was probably long after the solution had developed its maximum pressure.

Attention is called to the fact that the time within which the highest pressure is developed appears to be wholly independent of the concentration of the solution.

Column 8, Table XXXI., gives the maximum changes of temperature of the water—and, consequently of the solutions while the cells were in the bath, and column 9 gives the time over which these changes extended, *i. e.*, the time interval between the highest and lowest temperatures of the bath. The greatest change of temperature during an experiment was $0^{\circ}.65$, but, as this was gradual and extended over 26 hours, no "thermometer effects" were to be feared. On three other occasions the changes of temperature equalled or exceeded $0^{\circ}.5$. These variations ($0^{\circ}.65$, $0^{\circ}.56$, $0^{\circ}.54$ and $0^{\circ}.5$) are unnecessarily large under our present conditions, and they were

due, in each case, to a neglect of some of the arrangements by means of which we seek to maintain approximately constant temperatures in the bath while an experiment is in progress.

2. Table XXXII. *Summary of Results.* The method by which some of the values given in this table have been computed requires explanation.

Column 3 gives the lowest and highest temperatures of the water-bath during the several experiments. It is the differences between these which appear in column 8 of Table XXXI. The solutions in the cells are presumed to have the same temperatures as the water in the bath.

The values given in column 4, under the head of "Observed osmotic pressure," are mean values and they have been computed by adding the quantities given under "Osmotic pressure corrected," Tables IV. to XXX., and dividing the sum by the number of recorded observations. They represent quite exactly the mean, experimentally determined, osmotic pressure of the various solutions at the mean of the temperatures recorded in column 3.

The corresponding theoretical gas pressures, at the same temperatures, are given in column 5. These, like the "observed osmotic pressures" in column 4, are mean values which have been computed from the data given under "theoretical gas pressure" in Tables IV. to XXX.

In column 6 appear the minimum and maximum differences, for each concentration, between the observed osmotic pressure and the theoretical gas pressure. They are taken from the columns which are designated in Tables IV. to XXX. by the title "difference between pressure found and calculated," and are not mean values.

In connection with the molecular weights calculated from the observed osmotic pressure (columns 7 and 8), attention is called to the fact that, with one exception, they are much nearer to the theoretical value than are those which we are accustomed to obtain by the other so-called physical methods. The exception referred to is the case of the 0.1 weight-normal solution. The molecular weights found in this instance were 327.85 and 322.56, with a mean value of 325.21, which differs

from the theoretical molecular weight of cane sugar (339.6) by 14.39 units, or 4.26 per cent. No good reason is known for excluding that determination, and it is given with the others, notwithstanding the fact that much better results for the same concentration were obtained last year—namely, 337.0 and 336.6.

The effect of a given error in the measurement of osmotic pressure upon the computed molecular weights varies inversely as the concentrations of the solutions. This is made apparent by the following table, which gives, for each concentration, the effect in units, at 20°, of an error of 0.1 atmosphere upon the estimated molecular weight of cane sugar :

Weight-normal concentration.	Effect of 0.1 atmosphere upon molecular weight.
	Units.
0.1	14.21
0.2	7.11
0.3	4.74
0.4	3.55
0.5	2.84
0.6	2.37
0.7	2.03
0.8	1.78
0.9	1.57
1.0	1.42

It will be seen from the foregoing table that extreme care is necessary in order to obtain good molecular weight determinations by measuring the osmotic pressure of dilute solutions.

The difficulty which is peculiar to the measurement of the pressures of concentrated solutions is the large effect of small errors of calibration, or of reading, or of correction for meniscus. This will be illustrated by reference to Table XXXII. It will there be seen (column 6) that in the case of the two determinations of the osmotic pressure of weight-normal solutions the maximum deviations of observed from theoretical values were +0.3 atmosphere (No. 1) and -0.23 atmosphere (No. 2). These deviations, though seemingly large, are just about equivalent to the errors of meniscus in these measurements.

Our results are presented in their final form in Table

XXXIII., which differs from Table XXXII. only in that the extremes of temperature values (column 3, XXXII.) have been averaged and the extreme deviations of osmotic from gas pressure (column 6, XXXII.) have been replaced by the differences between the mean observed osmotic pressure and the mean calculated gas pressure.

If the mean of all the results is taken, the molecular weight of cane sugar is found to be 337.59, which differs from the theoretical value (339.6) by 2.01 units, or 0.59 per cent.

If the results obtained by the measurement of the pressure of the 0.1 weight-normal solution are excluded, and the mean of the remainder is taken, the molecular weight is found to be 338.82, which differs from the theoretical value by 0.78 unit, or 0.23 per cent.

These results are probably as precise as we can hope to obtain under present conditions. In our judgment they suffice to establish the conclusion which was deduced from the earlier series of measurements, namely, that *cane sugar in aqueous solution exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature, and the volume of the gas were reduced to that of the solvent in the pure state.*

It will be shown later that the same conclusion holds good for glucose.

For the present it must remain undecided whether the standard for the *volume of the solvent in the pure state* is its volume at maximum density, or at the prevailing temperature. This problem cannot be solved by the measurement of the osmotic pressure of cane sugar solutions, owing to the magnitude of the uncertainties which are due to inversion. If a substance can be found which undergoes no chemical change in the cell, and whose concentration of solution can be accurately ascertained, the question as to which volume of the solvent is the correct one for comparison can be answered; for, with such a substance, measurements of osmotic pressure could be made with a precision nearly equal to that which is required of an atomic weight determination.

It is hoped that we may be able, later, to extend the work upon cane sugar by taking up the measurement of pressure in

Table XXXIII.—Final Summary of Results.

Weight-normal concentration.	No. of experiment.	Temperature of solution.	Observed osmotic pressure. Atmospheres.	Theoretical gas pressure at same temperature. Atmospheres.	Differences between osmotic and gas pressure. Atmospheres.	Molecular weight calculated from osmotic pressure.	Mean molecular weight for each concentration.
0.1	1	24° 05	2.51	2.42	+0.09	327.85	325.21
	2	24° 23	2.55	2.43	+0.12	322.56	
0.2	1	20° 90	4.72	4.79	-0.07	344.96	341.87
	2	21° 47	4.78	4.80	-0.02	340.90	
	3	21° 75	4.81	4.81	0.00	339.74	
0.3	1	21° 65	7.24	7.21	+0.03	338.37	338.29
	2	19° 90	7.20	7.16	+0.04	338.20	
0.4	1	21° 62	9.64	9.61	+0.03	338.73	338.12
	2	22° 15	9.69	9.63	+0.06	337.50	
0.5	1	22° 60	12.06	12.06	0.00	339.59	337.89
	2	23° 70	12.22	12.10	+0.12	336.19	
0.6	1	24° 35	14.74	14.55	+0.19	335.32	335.24
	2	24° 23	14.70	14.55	+0.15	336.07	
	3	24° 1	14.77	14.54	+0.23	334.32	
0.7	1	23° 68	16.95	16.94	-0.01	339.59	339.55
	2	24° 03	16.96	16.93	+0.03	339.50	
0.8	1	23° 59	19.30	19.35	-0.05	340.48	339.78
	2	23° 68	19.39	19.36	+0.03	339.08	
0.9	1	24° 78	21.82	21.86	-0.04	340.19	339.51
	2	24° 78	21.91	21.86	+0.05	338.82	
1.0	1	23° 58	24.42	24.19	+0.23	336.39	339.56 ⁽⁸⁾
	2	24° 55 ⁽³⁾	24.05 ⁽⁴⁾	24.28 ⁽⁵⁾	-0.23 ⁽⁶⁾	342.72 ⁽⁷⁾	

the vicinity of 0° , and also that of more concentrated solutions.

The Depression of the Freezing Points of Cane Sugar Solutions.

In the earlier communication¹ attention was called to the fact that if the factor of density is taken into account, the apparent abnormality of the freezing points of cane sugar solutions disappears, in the sense that all concentrations of solution then conform to a general rule. The rule was formulated as follows: If Δ_1 represents the calculated depression of the freezing point, Δ its observed value, D the density of the solution at the temperature of freezing, and N its weight-normal concentration, then

$$\Delta_1 = 1.85 N D = \Delta \text{ for all concentrations.}$$

The rule was found to hold for all concentrations up to that of a gram-molecular weight of sugar dissolved in 1,000 grams of water; but, as the results upon which it was based were somewhat hastily obtained, and since the thermometer which was used had not been tested as to its accuracy, it was thought desirable to repeat the work with greater care and under more favorable conditions. This has been done.

The thermometer used in the later work is graduated in $0^{\circ}.01$ from $+1^{\circ}.0$ to $-5^{\circ}.0$, and its errors have been determined at the "*Reichsanstalt*." Before employing the instrument, it was tested as to a possible continued shrinkage of the bulb. It was found that the 0° point had suffered an upward displacement, amounting to $0^{\circ}.02$, since the date of the *Reichsanstalt's* certificate, which, of course, was taken into account in applying corrections for the certified errors of the thermometer.

The densities of the solutions were determined in pycnometers, which were modified somewhat in form, to enable us to ascertain with a fair degree of certainty the temperature of minimum volume.

We cannot predict *which density* of solutions, if any, will be found to have a definite relation to their freezing points; accordingly, the specific gravities of the cane sugar solutions

¹ THIS JOURNAL, 34, 93.

were determined: (1) at the freezing point of the solvent, *i. e.*, 0° , (2) at the freezing temperature of the solution, and (3), as far as practicable, at the temperature of minimum volume, *i. e.*, maximum density.

No great degree of accuracy can be ascribed to the determinations of temperatures of maximum density, though they are believed to be fairly correct. The greatest difficulty which was experienced in this connection was due to the fact that, in the case of the 0.5 normal, and of more concentrated solutions, the temperature of maximum density is considerably below that of freezing. On this account great caution was necessary, in some instances, in order to secure the requisite amount of undercooling before the formation of ice set in. In the case of the normal solution it could not be done, and the temperature of minimum volume of that concentration could only be conjectured from the values which had been obtained for less concentrated solutions.

The data which were gathered in the course of the work upon the densities and the freezing-points of cane sugar solutions are brought together in the following tables. For the present, they serve no very obvious purpose except to confirm the rule for cane sugar which was expressed by the equation $\Delta_1 = 1.85 ND = \Delta$. It appears to the authors desirable to ascertain *experimentally* (rather than by an exercise of the speculative faculty) whether the same or any other definite relation exists between the densities and the so-called *abnormal freezing points* of other solutions. The rule does not hold good for glucose, but the freezing points of glucose solutions are *normal* in the sense that the magnitude of the depression is strictly proportional to the weight-normal concentration.

If the densities of solutions which exhibit abnormalities of freezing points are found to be connected in some definite way with those abnormalities, it requires no great exercise of the imagination to predict that a similar relation will be found to hold between the vapor tension and the densities of the same solutions, but the normal procedure would seem to be, first to establish the fact, and then to seek for the reason.

Table XXXIV.—Density of Cane Sugar Solutions.

Weight-normal concentration.	Temperature of maximum density.	Density at temperature of minimum volume.	Density at freezing point of the solution.	Density at freezing point of the solution.
0.1	+4°.2	1.01310	1.01310	1.01309
0.2	+3°.2	1.02570	not determined	1.02574
0.3	+1°.0	1.03787		1.03787
0.4	—0°.4	1.04953		1.04951
0.5	—1°.9	1.06079		1.06067
0.6	—3°.7	1.07160		1.07136
0.7	—5°.0	1.08204		1.08167
0.8	—6°.0	1.09204		1.09156
0.9	—7°.5	1.10175		1.10107
1.0	not determined	1.11114 ¹		1.11025

Table XXXV.—Observed and Calculated Freezing Points of Cane Sugar Solutions.

Weight-normal concentration.	Observed depression of the freezing point.	Calculated values of 1.85 N.D. ²	Difference between actual and calculated depression.	Molecular lowering of freezing points.
0.1	0°.195	0°.187	0°.008	1°.95
0.2	0°.393	0°.380	0°.013	1°.96
0.3	0°.584	0°.576	0°.008	1°.95
0.4	0°.784	0°.777	0°.007	1°.96
0.5	0°.983	0°.981	0°.002	1°.97
0.6	1°.190	1°.189	0°.001	1°.98
0.7	1°.390	1°.401	—0°.011	1°.99
0.8	1°.621	1°.616	0°.005	2°.02
0.9	1°.829	1°.834	—0°.005	2°.03
1.0	2°.066	2°.056	0°.010	2°.07

It is customary at the present time to ascribe the abnormally great depression of the freezing points of certain concentrated solutions to an appropriation, by the dissolved substance, of a portion of the solvent, which is attended (if it really occurs) by a corresponding concentration of the solution. In this way the eccentricities of the freezing points of cane sugar solutions have been explained; but the authors feel called upon to point out one fact which is not easily reconciled with this explanation, namely, the fact that there are no corresponding irregularities in the *osmotic pressures* of cane sugar solutions. Within the limits of unavoidable experimental errors, the os-

¹ Calculated.² Density at minimum volume.

otic pressures of cane sugar solutions have been found to be proportional to their supposed concentrations, which could hardly be the case if the sugar had abstracted from the solvent the quantities of water necessary to account for the aberrations of the freezing points.

The depression of the freezing-point of a 0.1 weight-normal solution of cane sugar is $0^{\circ}.195$, while that of the normal solution is $2^{\circ}.066$ instead of $1^{\circ}.95$. In other words, the depression of the freezing-point of the weight-normal solution is *abnormal* to an extent not less than $0^{\circ}.116$, the equivalent of which, in osmotic pressure at 24° , is approximately 1.44 atmospheres. If, then, the sugar in a weight-normal solution withdraws enough water from the solvent to produce an abnormal depression of the freezing point amounting to $0^{\circ}.116$, we should have found, for that concentration, an osmotic pressure of 25.67 atmospheres instead of 24.23 atmospheres, which is the mean value of all our determinations, with a maximum deviation from this value, among the individual determinations, amounting to about 0.25 atmosphere. These figures, since they represent mean values, are not exact, but they are correct to within 0.02 or 0.03 of an atmosphere.

It may be surmised that, at the comparatively high temperatures at which our measurements were made, the *whole* of the water does in reality play the part of solvent, while, at lower temperatures, a portion of it is appropriated by the sugar, giving rise to a concentration of the solution and, consequently, to an abnormal depression of the freezing point.

While, in general, we would deprecate free speculation until after many more facts relating to osmotic pressure have been *experimentally* established, this provisional reconciliation of the contradictions between freezing point depressions on the one hand, and osmotic pressure on the other, appears to have in it enough of plausibility to make desirable a determination of the osmotic pressure of cane sugar solutions at *low* temperatures, and this will be undertaken in the near future. If the supposed abstraction of water from the solvent takes place within the range of low temperatures at which we find it practicable

to work, we may expect to find evidence of it in the form of abnormally high osmotic pressures.

JOHNS HOPKINS UNIVERSITY,
May 25, 1906.

REPORTS.

The Change of Oxygen into Ozone at a High Temperature, and the Oxidation of Nitrogen.

Under this title Franz Fischer and Fritz Braehmer have recently published an interesting article,¹ of which the following is an abstract:

Ozone, like nitric oxide and hydrogen peroxide, is an endothermic compound, it should, therefore, be readily formed at high temperatures and should be stable at its temperature of formation.

The conditions for the production of nitric oxide from the air are known.² Nernst³ has calculated the concentration-equilibrium for different temperatures.

Table I.— $N_2 + O_2 \rightleftharpoons 2NO$.

T (absol.).	$\theta = ^\circ C.$	NO observed.	NO calculated.
1811	1538	0.37 vol. per cent	0.35
2033	1760	0.64	0.67
2195	1922	0.97	0.98
3200	2927	5.00 approx.	4.4

The speed of formation is relatively slow. Nernst has computed the following values for the time in which one-half of the possible nitric oxide concentration occurs when air is heated: At 1200° very long; 1538° , 97 seconds; 1737° , 3.5 seconds; 2600° , 0.0018 seconds. As the speed of decomposition corresponds to the speed of formation, the possibility of cooling the NO to lower temperatures without especial precaution is apparent.

Moritz Traube⁴ formed hydrogen peroxide at high temperatures by directing a jet of burning hydrogen on water or ice, the sudden cooling preserving the peroxide intact and enabling him to isolate it from the mixture of hydrogen, oxygen, water and hydrogen peroxide existing at 2400° .

¹ Ber. d. chem. Ges., 39, 941 (1906).

² Vide Brode's Monograph, "Oxidation des Stickstoffs in der Hochspannungsflamme," von Johannes Brode, Halle: Knapp, 1905, and a recent report in this JOURNAL "On the Oxidation of Atmospheric Nitrogen." THIS JOURNAL, 35, 358.

³ Nernst: Nachr. kön. Gesell. Wiss. Göttingen, 1904, 261.

⁴ Ber. d. chem. Ges., 18, 1890.

The following table contains Nernst's¹ calculations for the percentage of hydrogen peroxide which can co-exist with water vapor and oxygen at given temperatures and 0.1 atmosphere pressure :

Table II.— $2\text{H}_2\text{O} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}_2$.

T (absol.).	$\theta = ^\circ\text{C}.$	Per cent H_2O_2 .
2784	2511	0.66
2154	1881	0.24
1493	1220	0.028
1140	867	0.0032
923	650	0.00036

As the temperature of the hydrogen flame is much above 2000° it must contain hydrogen peroxide, and Traube found experimentally 0.74 per cent.

The values which Nernst² has calculated for the speed of decomposition of hydrogen peroxide are very close to those which were determined by Clement for ozone.

In the following table Nernst gives the figures calculated for the percentage of ozone, which can exist in equilibrium with oxygen at different temperatures :

Table III.— $3\text{O}_2 \rightleftharpoons 2\text{O}_3$.

T (absol.).	$\theta = ^\circ\text{C}.$	Vol. per cent O_3 .	Weight per cent O_3 .
1569	1296	0.1	0.15
2321	2048	1.0	1.52
4773	4500	10.0	16.50

Clement found that at given temperatures the speed of decomposition of ozone is several million times greater than that of nitric oxide, while at 1000° an ozone-oxygen mixture, containing 1 per cent of ozone, drops to 0.001 per cent in 0.0007 second ; the speed of decomposition of nitric oxide at that temperature is very small.

To sum up, we see that for nitric oxide and hydrogen peroxide theory and experiment agree qualitatively, for nitric oxide quantitatively.

As to the formation of ozone at high temperatures, it had not been experimentally proved before the present work ; for though many chemists, among whom were Schönbein, Böttger, Struve and Traube, believed that they detected the odor of ozone when hydrogen burned, other chemists denied this and said that the odor and reactions were due to oxides of ni-

¹ Z. physik. Chem., 46, 722.

² Z. elek. Chem., 11, 713.

trogen or to hydrogen peroxide. Other experimenters thought that they detected the odor of ozone when air or oxygen was passed over glowing platinum.

Clement,¹ in his second series of experiments, found that under the conditions at which previous observers had worked, ozone could not be detected, but nitric oxide or nitrous anhydride was obtained, which, in great dilution, has the odor of ozone and acts in the same way on most reagents. Clement used Arnold and Mengel's² "tetra-base" paper, *i. e.*, paper soaked in an alcoholic solution of tetramethylpara, diaminodiphenylmethane. Ozone colors this paper violet, nitric oxides pale yellow, while hydrogen peroxide does not affect it. Clement also worked with Nernst filaments at 3000° and could detect no ozone. In short, the only case where he did detect it was in the action of electric sparks on air, but in this instance it is probable that the ozone was formed by the action of the ultra-violet rays from the spark and not by thermal action.

From the facts thus far enumerated, Fischer and Braehmer concluded that to obtain ozone from heated oxygen one must cool the heated gas more quickly than the ozone could decompose.

They have accomplished this by heating oxygen in various ways in *liquid oxygen* or *liquid air*. The oxygen may be heated by burning hydrogen or other gases, by a glowing object, or by sparks, as detailed below.

The apparatus used in burning hydrogen in liquid air or oxygen is shown in Fig. I. It consists of a test tube 18x4 cm., closed with a cork stopper. In the cork are three tubes; the bent tube *a* is to conduct the outflow of gas into water; the tube *b* is for filling the apparatus with liquid air or liquid oxygen. The tube *c*, through which the hydrogen is introduced, is prolonged by a quartz tube 10 cm. long, reaching nearly to the bottom of the test tube; the test tube is placed in a Dewar bulb. For an experiment both the unstoppered test tube and Dewar bulb are filled with pure liquid air, the test tube being two-thirds full. A current of pure, dry hydrogen is passed through tube *c* and ignited; the current is so regulated that the flame is about 1 cm. long; now the hydrogen flame is plunged into the test tube of liquid air till the cork fits tightly; the flame burning in the liquid air causes the latter to boil away rapidly; in 2-3 minutes it nearly boils out of the tube; the flame is withdrawn from the tube before it is exposed by the liquid boiling away.

The gas escaping from the tube through *a* had the odor of

¹ Ann. Phys., 14, 334.

² Ber. d. chem. Ges., 38, 1324.

ozone, but gave no ozone reactions; the surface of the liquid air remaining in the tube was covered with a bluish snow; on

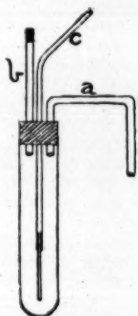


Fig. I.

filtering, it remained on the filter and was proved to be frozen nitric oxide; the characteristic and delicate test for hydrogen peroxide with titanous acid failed to show any trace of this substance. The filtrate was poured into a porcelain crucible and allowed to boil away; a strong odor of ozone was noticeable, "tetra-base" paper held over the crucible turned violet, and as the last of the air boiled off, dark blue rings of pure liquid ozone were left.

Control experiments, made by boiling off liquid air alone showed that the liquid air used contained no trace of ozone.

The experiment proves that nitric oxide and ozone, but no hydrogen peroxide, are formed when hydrogen is burned in liquid air, and that, by rapid cooling, it is possible to preserve the ozone dissolved in the liquid air, and easily separate it from the frozen oxides of nitrogen. While only NO is formed at high temperatures, on cooling—through oxidation—mixtures of gaseous NO and NO_2 would result, yielding, at a low temperature, solid N_2O_3 .¹

The following substances were burned in—or in contact with—liquid air:

- Carbon monoxide: Yield, solid carbon dioxide, solid nitrous anhydride, liquid ozone.

Acetylene: Yield, carbon, carbon dioxide, nitrous anhydride and ice as solids, liquid ozone.

¹ THIS JOURNAL, 35, 358.

Hydrogen sulphide: Yield, hydrogen sulphide, sulphur dioxide, water as solids, traces of liquid ozone.

Burning sulphur: Yield, sulphur dioxide, nitrous anhydride as solids, liquid ozone.

Glowing charcoal: Yield, carbon dioxide, nitrous anhydride as solids, liquid ozone.

Glowing splinter of wood: Yield, carbon, carbon dioxide, nitrous anhydride and water as solids, liquid ozone.

In none of these reactions was hydrogen peroxide formed.

Hydrogen burned in pure, liquefied, electrolytic oxygen, in an apparatus arranged to exclude air, yielded ozone only.

Another portion of the same oxygen was boiled off and was proved to contain no ozone.

A platinum wire heated by an electric current was plunged into liquid air; as soon as the layer of gaseous air (Leiden-frost phenomenon) had formed around the wire, the latter became white-hot, indicating a temperature of about 1700° ; only ozone was formed.

This experiment proves that, at temperatures below the melting point of platinum, nitric oxide is not formed from liquid air, while ozone is produced.

A Nernst filament, heated by a current of 0.5 ampere and 220 volts, plunged in liquid air or in liquid oxygen, yielded ozone only; here, as with the platinum wire, the temperature was not high enough for nitric oxide to form.

On arranging an apparatus so that an arc was formed between platinized copper terminals in liquid air, solid oxide of nitrogen and liquid ozone were produced.

The ozone formed by the arc exploded; that formed by the platinum wire or Nernst filament was not explosive. The authors ascribe the explosiveness of ozone, therefore, to traces of oxides of nitrogen dissolved in it.

The formation of nitric oxide, as already proved by others, is purely thermal; the formation of ozone is generally thermal, though in case of the arc and still more in case of sparks, it is probable that the photochemical action of the ultraviolet light has a large share in its production.

To determine whether heat or light caused the action when the Nernst filament was used, the following two experiments were performed. 1. A Nernst filament was put in a closed quartz tube, the pressure in the tube reduced to 12 mm., the current turned on, and the tube containing the glowing filament plunged into liquid air in an apparatus similar to that in Fig. I. The air boiled gently but no ozone was formed in the liquid air; that ozone is formed if enough heat passes through

the quartz is proved by Experiment 2, in which a quartz U-tube was filled with hydrogen at 3 mm. pressure and the discharge from a small induction coil passed through it; when it was plunged into the liquid air ozone was at once formed outside the quartz tube, as a part of the short wave heat rays, produced within the tube, passed through the quartz and ozonized the oxygen. In the first experiment the heat rays from the glowing filament had to pass through an air cushion of 12 mm. pressure and 0.5 cm. thickness, hence did not pass through the quartz. Warburg and Regener¹ have shown that ozonizing light rays are not readily absorbed by air or oxygen, so that if the ozonization by the glowing Nernst filament depended entirely, or in part, on ozonizing light rays, ozone should have been formed in Experiment 1.

It is well known that hydrogen peroxide is produced by rapidly cooling the products of combustion of hydrogen; yet the authors found no trace of hydrogen peroxide after burning hydrogen in liquid air or in liquid oxygen; they suggest the following explanation: The formation of ozone, of nitric oxide and of hydrogen peroxide, must be preceded by a dissociation of molecular oxygen, $O_2 \rightleftharpoons O + O$. The speed of reaction in the formation of ozone and hydrogen peroxide being approximately equal, in the experiments in liquid air or oxygen, where combustion occurs in presence of a large excess of oxygen, many more molecules of oxygen will be oxidized to ozone than water molecules to hydrogen peroxide. Further, in the moment of cooling, ozone may react on hydrogen peroxide, $O_3 + H_2O_2 = H_2O + 2O_2$, thus using up the relatively small amounts of hydrogen peroxide formed.

The authors studied the quantitative relations of the ozone formation, choosing as their method the action of the Nernst filament on liquid oxygen. The apparatus is shown in Fig. II. The Nernst filament is horizontal between the ends of the electrodes; the capillary tube A dips into mercury. About 30 cc. of pure liquid oxygen are put in the test tube; as soon as the tube is closed by the glass stopper carrying the electrodes and glowing Nernst filament, oxygen begins to escape through the capillary tube; but a Dewar bulb B, filled with liquid air, is instantly placed around the test tube, thus cooling the liquid oxygen below its boiling point so that none can escape. On the contrary, there was a diminution of pressure equivalent to 250 mm. of mercury.

In four experiments the Nernst filament was kept 25, 50, 125 and 360 minutes, respectively, in the liquid oxygen. The

¹ Sitzungsber. K. preuss. Akad. Wiss., 1904, p. 1228.

ozone formed was determined by changing the glass stopper for one carrying a tube connecting with an absorption appara-

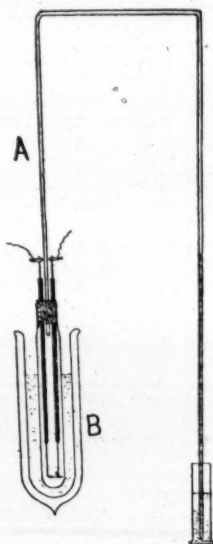


Fig. II.

tus filled with potassium iodide solution; the ozone solution was allowed to boil off, the gasified ozone swept out by a current of compressed air, and the iodine set free was determined. The following table gives the results:

Time. Minutes.	Mg. O ₂ .	Solution vol. cc.	Solution. Grams.	Weight per cent O ₂ .
25	40	30	33.6	0.12
50	76	32	35.8	0.21
125	159	30	33.6	0.47
360	322	30	33.6	0.96

If a curve is plotted using the time in minutes as abscissae and the percentages of ozone as ordinates, a glance at the figures shows that the percentage of ozone formed does not in-

crease with the time, but much more slowly; a stationary condition had not been reached in 360 minutes, which is the limit of the authors' experimental data, but their study of the curve leads them to believe that an ozone-oxygen equilibrium is reached at 1.5 per cent, *i. e.*, that the ozone concentration will not increase beyond 1.5 per cent at the temperature of the Nernst filament.

On comparing these figures with those calculated by Nernst in Table III., assuming that the Nernst filament gave a temperature of 2048° , which is probably about correct, and assuming that the maximal concentration which the authors calculate by graphic extrapolation of their curve is accurate, there is close agreement between the experimental result and Nernst's figures, which give the absolute temperatures calculated from the electromotive energy of the ozone-oxygen couple for different relations of concentration of oxygen to ozone.

The authors calculate that by this method 3.5 grams of a 0.12 solution of ozone is made per kilowatt hour, while the ordinary method of preparing ozone by the silent discharge yields 15 grams ozone in 3-4 per cent solution, per kilowatt hour.

E. RENOUF.

An Investigation to Determine whether there is Change in Weight in Chemical Reaction.

The classical work of Landolt¹ on this problem is well known. Since his earlier results were published a number of investigations have been carried out along the same line. Landolt has now extended his earlier experiments, and the object of this note is to give a brief review of what he has done and what results he has obtained.

For the former work Landolt had at his disposal one of the finest chemical balances that had ever been constructed up to that time. It was capable of weighing 500 grams to within a few thousandths of a milligram, or at most a hundredth of a milligram.

The solutions of the two substances that were to be allowed to act upon one another were placed each in one arm of an inverted U-tube. Another U-tube of very nearly the same weight and external surface was used as a tare. After the first double weighing had been effected, the solutions were brought together by tilting very slowly the inverted U-tube. This was to prevent the reaction from proceeding rapidly and producing large changes in temperature in the containing vessel.

This earlier work of Landolt was a model of care and pre-

¹ Z. physik. Chem., 12, 1, 1903.

caution, and every conceivable source of error was taken into account. In this manner the following reactions were studied :

- I. $\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$;
- II. $\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$;
- III. $2\text{I} + 2\text{Na}_2\text{SO}_3 = 2\text{NaI} + \text{Na}_2\text{S}_2\text{O}_4$;
- IV. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O} + \text{KOH} = \text{CHCl}_3 + \text{CHO} \cdot \text{K} + \text{H}_2\text{O}$;
- V. $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O} + \text{water} = \text{solution}$.

In nearly all cases the changes in weight that were found were larger, and much larger than the sum total of the known experimental errors. In *nearly all cases there was a loss in weight*. This amounted to as much as 0.177 of a milligram, while the experimental error was from 0.01–0.02 of a milligram. In a very few experiments a gain in weight was found, but this was nearly always very small, being of the order of magnitude of the experimental error.

Of the various investigations carried out after this earlier work of Landolt, that of Heydweiller¹ deserves very special mention. His work, like that of Landolt, was a model of accuracy in every respect.

He studied the following six reactions :

- I. The action of iron on copper sulphate.
- II. Solution of copper sulphate in water.
- III. Mixing copper sulphate with dilute sulphuric acid.
- IV. Mixing of copper sulphate with potassium hydroxide.
- V. Action of acetic acid on ammonia.
- VI. Action of sulphuric acid on barium chloride.

Heydweiller found changes in weight of the same order of magnitude as those found earlier by Landolt, and an important point is that, with the exception of two experiments, the change in weight was always negative—there was a *loss in weight during the reaction*.

Landolt, being provided with a new and improved balance, took up the problem again in 1901, and the results of this last work have just been published.² In these new experiments greater precautions, if possible, are taken than in the earlier investigation. It would lead too far to discuss these in any detail. The effect of change in temperature on the balance, and on the vessels containing the solutions, the position of the vessels on the arms of the balance, the effect of warming the vessels by the heat liberated during the reactions, the deposi-

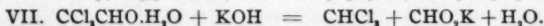
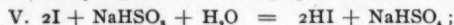
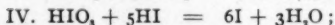
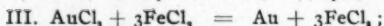
¹ Ann. d. Phys. (Drude), 8, 304 (1901).

² Sitz. d. kön. preuss. Akad. d. Wiss., Feb. 15, 1906.

tion of moisture on the surface of the vessels, the change in the volume of the solutions effected by the reactions, are some of the matters that were taken into account.

To determine the maximum experimental errors that were possible, experiments were carried out by introducing into the vessels substances that would not react chemically with one another. The errors were found to be, at most, of the order of magnitude from 0.01-0.02 of a milligram.

The reactions which Landolt has studied in this later work are the following :



VIII. Electrolysis of cadmium iodide.

To give an idea of the character of the results obtained by Landolt, his figures in the case of one reaction—the first—are given :

Observed changes in weight. Milligram.	Error in weighing. Milligram.
-0.085	0.009
-0.103	0.009
-0.068	0.010
-0.042	0.009
-0.029	0.009
-0.199	0.030
-0.137	0.028
-0.079	0.013
+0.003	0.004
-0.003	0.009

In some of the reactions the changes in weight found experimentally were scarcely larger than the experimental errors.

However, wherever appreciable changes in weight were found, they were always negative. That is, *whenever there was a change in weight, there was always loss in weight*, and the amount of the loss was of the order of magnitude indicated by the above results.

A relation of this kind is obviously of very great importance.

It raises the question as to whether the law of the conservation of matter holds rigidly when chemical reactions take place. The evidence for the existence of such a law is based, primarily, upon weight remaining unchanged when chemical reaction occurs, and in the determination of this factor we are, obviously, bound by the limit of error of our experimental work.—It seems, from this most refined investigation, that there is frequently slight loss in weight when chemical reactions take place.

Landolt attempts to account for this loss in weight, as we might imagine, in terms of the electron theory. He suggests that during chemical reaction the atoms are probably subjected to violent agitation, and it is quite conceivable that some electrons might be set free from the atoms and escape. These might easily pass through the walls of the containing vessels, thus reducing the mass of the reacting substances.

If this is the true explanation of the loss in weight in chemical reaction, then, as Landolt suggests, we should expect to obtain different losses in weight when the containing vessel had thick walls than when the walls were thin. Further, the loss would be different when different substances were used for constructing the vessels. These conditions remain for investigation in the future.

In terms of the electron theory of J. J. Thomson, it is quite conceivable that some electrons would be shot off during chemical reactions, and that the law of the conservation of mass, as usually understood, does not hold rigidly when substances are allowed to react with one another chemically.

This raises the further question, are any of our so-called laws of nature really rigid generalizations? We know that very few of them are, the number gradually decreasing as experimental work becomes more and more refined. It would scarcely be surprising to find that the best of them are only close approximations.

H. C. J.

REVIEWS.

ADOLF VON BAEYER'S GESAMMELTE WERKE. Herausgegeben zur Feier des siebenzigsten Geburtstages des Autors von seinen Schülern und Freunden. Braunschweig: Fr. Vieweg und Sohn. 1905. Band I., pp. cxxxii + 990; Band II., pp. 1196. Price, M. 16.

The collected works of Nencki were reviewed some little time ago,¹ now we have those of Baeyer, issued by a committee in celebration of his seventieth birthday and edited by Dr.

¹ THIS JOURNAL, 34, 352 (1905).

V. Villiger. It is to be hoped that this indicates a growing fashion, as the custom of issuing the collected works of the leaders of science during their lifetime is entirely admirable. One of the most valuable features of the present book is a brief autobiography, which it is difficult to praise too highly. It is most fascinating reading, giving, as it does, a clear, simple and thoroughly modest account of the writer's struggles, difficulties and successes; moreover, his mention of other great men with whom he came in contact is natural and unforced, it is never disparaging, he always gives praise where it is due but, on the other hand, there is entire freedom from that conventional eulogy which is as common as it is wearisome.

Johann Friedrich Wilhelm Adolf Baeyer was born October 31, 1835, in Berlin. Hitzig, his maternal grandfather, in addition to his position in the criminal judicature, stood high in the literary circles of Berlin on account of his biographical writings; his uncle, Franz Kugler, was the art historian, and his father was in the General Staff, at that time captain, later rising to the rank of lieutenant-general. When a small boy, Adolf Baeyer passed his holidays with his father, who was engaged in geodetic surveys, and spent days amusing himself with such flowers or animals as he could find, thus becoming accustomed to original, close observation. A better training for any child could hardly be conceived. Baeyer entered chemistry by the firework route and, to avoid worse things, on his ninth birthday his father gave him a copy of Stöckhardt's "*Schule der Chemie*." With his pocket money of 12½ cents weekly, he fitted a room as a laboratory, worked through all the experiments and gave lectures to a boy friend, who, in return, cleaned the apparatus. It is interesting to remember that Ostwald has recently stated that he was also first attracted to chemistry by the study of Stöckhardt's book; such a record is probably unique. Baeyer's earliest original discovery was made at this time; he prepared the compound $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$, from copper sulphate and sodium carbonate. E. Mitscherlich, who was visiting at the house, was shown the crystals and stated that they were novel, but Baeyer had no analytical balance and no knowledge of how to publish new observations; four years later the compound was described by Struve.

During his thirteenth year Baeyer left the Friedrich Wilhelm Gymnasium and entered Schellbach's School of Natural Science and Mathematics. Here his interest in chemistry received a powerful stimulus, especially in connection with uric acid and indigo, but he was also much attracted to mathe-

matics and physics; however, by the time he was 15 years of age botany had supplanted all three of these subjects in his esteem.

At the University of Berlin Baeyer thoroughly enjoyed himself, in company with von Richthofen, Weingarten, Paalzow, Ernst Haeckel and Paul Ascherson; he studied physics under Magnus and, although not prone to attend lectures, he made an exception in the case of those of Dirichlet on mathematics. After his one year military service, Baeyer was weary, nothing interested him but chemistry, so he decided to become a chemist and went to Bunsen, at Heidelberg, in 1856. Evidently his previous work had been good, for after a summer semester at analysis, he was started on a research on the reaction of bromine and tartaric acid, a part of the photochemical work of Bunsen and Roscoe; Baeyer says of this that the work was purely mechanical and the ideas which he expressed in the published paper were Bunsen's. Later, the assistant Pabal, who had been requested by Bunsen to investigate the various methyl chlorides, transferred the subject to Baeyer. One method of preparing methyl chloride was by heating cacodylic acid with hydrochloric acid. Consequently, at the end of the research, Baeyer was possessed of a considerable quantity of cacodylic acid. On showing it to the assistant Schischkoff and asking what he had better do with it he received the reply, "at present it is the fashion to treat everything with phosphorus pentachloride." This advice was followed with results that are well known. Evidently, too, "fashion" in chemistry is not so new as some users of the Grignard reaction might imagine.

In Bunsen's laboratory Baeyer learnt analysis and gasometric methods, but nothing else, for by that time Bunsen had entirely lost his interest in organic chemistry, consequently, in the spring of 1857, Baeyer went to Kekulé, who was then privatdocent at Heidelberg; it was here that cacodyl trichloride was prepared. Kekulé's laboratory consisted of a single room, without draught other than was afforded by the defective flue of a neighboring kitchen, the result was that one day he found Baeyer semi-delirious, with a greatly swollen face, due to the accidental inhalation of methylchlorarsine—surely a rather strenuous method of discovering a new compound and investigating its properties! Baeyer returned to Berlin at Easter, 1850, to obtain the Ph.D. degree; his dissertation included the results of his work on arsines and, as it had been conceived and executed entirely alone, he obviously deserved far more credit than the majority of candidates. The work was, how-

ever, not understood by Mitscherlich, H. Rose and Magnus, and although their attitude to him personally was paternal, as a candidate his reception was chilly. Eventually he received a second mark. It is instructive to compare this result and the quantity of research which Baeyer had done with present-day methods of producing Ph.Ds.

The winter of 1858-9 was spent with Kekulé at Ghent, work being commenced on uric acid derivatives. His efforts to prepare uric acid by the elimination of water from pseudouric acid failed, owing to the use of too concentrated mineral acid, as was shown, later, by E. Fischer.

The spring of 1860 saw Baeyer as "privatdocent," but without any laboratory and without the private means for fitting one. In the autumn, however, he became instructor of organic chemistry at the "Gewerbe-Institut," now the "Technischen Hochschule." The appointment was by no means an attractive one, it was terminable at 3 months' notice and the salary was M. 1800, say \$450 per annum, of which half had to be turned over to assistants, but a good laboratory was provided and the next 3 years were spent on the uric acid researches, in conjunction with Damm, Deichsel, Herzog and Heintzel. After the death of E. Mitscherlich, in 1863, and of H. Rose, in 1863, and pending the arrival in Berlin of A. W. Hofmann, in 1865, the lectures were given by several junior members of the University; Baeyer also secured the necessary permission to give a course and made the needful preparations, but not a single student attended!

In 1865 Baeyer was to have succeeded Kolbe in Marburg, but, over the head of his minister, the reigning sovereign appointed Carius. The following year, with Hofmann's support, Baeyer was made honorary "Extraordinarius," and in 1870 he received a call to Königsberg, as successor to Werther. This was declined because the laboratory was represented as being unhealthy, but, on the ground of having received the call, of having served faithfully for 10 years, and of the research work which had been done in his laboratory, he applied to the authorities for his appointment to be made permanent and for a small increase in salary, both requests received a brusque refusal. The discovery of artificial alizarin had been made in Baeyer's laboratory two years previously. In 1868 occurred his marriage with a daughter of Geheimrat Bendorff.

In 1872 it was proposed to appoint Baeyer as professor of pure chemistry in the medical faculty of the University of Berlin, the idea being to have one place in Germany where

medical students could obtain advanced instruction in chemistry. Naturally the faculty objected, because it was impossible for them to believe that any one who had not studied anatomy could possibly teach chemistry—to medical students. The same notion is still widely prevalent in this and other countries, in spite of the work of E. Fischer, a pure chemist, which has done more for physiological chemistry than that of any other single man. The proposal was, however, abandoned on account of the resignation of the minister of education. Among other students in Baeyer's laboratory at this time may be mentioned Liebermann, C. Graebe and Victor Meyer. In 1872 Baeyer was called to Strassburg and in the spring of 1875 he succeeded Liebig in Munich. The latter had stipulated, when he went there, that he should have no practical classes, hence Baeyer had to build and equip a laboratory, which was an advantage in so far as he was saved from taking over a quantity of useless material, of students and assistants. The inorganic work was given to Volhard, who was the only legacy from Liebig, and his methods of instruction have never been improved upon by his successors. The magnitude of this statement will be apparent when it is mentioned that his place was occupied, in turn, by E. Fischer, Clemens Zimmermann, v. Pechmann and G. Krüss; the methods are also in use in other German laboratories and in that of the Johns Hopkins University.

Baeyer concludes his recollections by some remarks on chemical education, the training of technological chemists and the evils of examinations. These last might well be taken to heart by the English authorities, whose practice is exactly the opposite to that advocated by Baeyer; the results to English chemistry are notorious. As regards the second subject, it may be said that the first and last essential is that the would-be technologist should be taught chemistry—in the broadest possible way. This has been accepted in Germany, its truth is beginning to be realized by "Captains of Industry" here, but in England they are, apparently, still as far as ever from recognizing it.

The description, by E. Fischer, of the life at Strassburg is, needless to say, delightful, witty and full of good stories. Unfortunately, space is lacking to reproduce them all. E. and O. Fischer had started on a tour from Bonn, thoroughly dissatisfied with the instruction in analysis which they had been receiving there, indeed, E. Fischer had almost decided to abandon chemistry in favor of physics. They came to Strassburg and met the "Inspector" (a kind of glorified janitor),

who proved to be most affable. Now they argued 'if the Inspector, who is well known to be *the* most important person in an institution, is agreeable to such a degree, to what dizzy height in this respect must not the assistants, and particularly the professor attain?' Therefore they remained. Bunsen's methods of analysis were taught by F. Rose, who had accompanied Baeyer from Berlin, and Fischer describes the fascination which quantitative analysis has had for him ever since. In those days it was not customary to make organic preparations, practical organic chemistry was learned by working with the substances to be used in the graduation work. Fischer, for example, began his research without having made a combustion or knowing how to distil ether. These and other matters the student acquired partly by the light of nature, often by the direction of a more senior student and, occasionally, from an instructor. Fischer was started on an investigation of hydromellitic acid; shaking machines had not been invented and he was walking about the laboratory, which was a temporary structure, with a bottle containing 0.5 kilo of mellitic acid and 25 kilos of mercury, his foot went through the floor board, with the result that half the mercury and the whole of the acid were lost, this, he says, 'suggested to Professor Baeyer the desirability of giving him another subject on which to work'. One would like to record the names of the students, instructors and professors who were then at Stassburg and relate some of their adventures, including that of Meer, who, because of his work on chlorphenol, was turned out of his dwelling and refused admission to any restaurant or boarding-house, fortunately for him, Mrs. Baeyer came to the rescue.

The discovery of phenylhydrazine is too good to be omitted. A student had been told to make diphenol from benzidine; he obtained only a tar. Doubtless, as is usual with students, he explained that he had done everything thinkable and that the result was due to the inherent perverseness of the material; doubtless, also, as is usual with organic instructors in such circumstances, Fischer did not attach any particular weight to his statements. At all events Fischer did the experiment himself and got a similar result! On consideration he decided that this was due to the oxidizing action of the nitrous acid, so he repeated the experiment in the presence of sodium sulphite and obtained crystals which were new to him and also to Baeyer. The substitution of aniline for benzidine gave him phenylhydrazine.

Following the autobiography, Baeyer gives an account of the leading ideas which have guided his researches; to compress it

would be an impertinence, it will suffice to say that it is of absorbing interest and should be read by every chemist. Such glimpses into the working of the mind of a great leader are invaluable. Baeyer's lecture on the synthesis of indigo, which was delivered on the occasion of the opening of the "Hofmann-Haus" in 1900, is also reproduced, then follows a list of all papers published from his laboratory. Although many of these do not bear his name, it is safe to say that all of them are indebted to him for criticism, advice, suggestion, or direct inspiration. This list occupies 63 pages.

The remainder of the volumes consists of Baeyer's own papers, which are grouped according to subject, into 19 sections, as follows: Organic arsenic derivatives, pp. 54; uric acid derivatives, pp. 124; indigo, pp. 184; researches connected with indigo, pp. 70; pyrrol and pyridine bases, pp. 38; dehydration and condensation, pp. 120; phthalein, pp. 220; the hydroaromatic compounds, degradation of mellitic acid and the constitution of benzene, pp. 488; researches on terpenes, pp. 270; nitroso-derivatives, pp. 60; furfuraldehyde, pp. 22; acetylene derivatives and the strain theory, pp. 48; peroxides, pp. 100; the basic properties of oxygen, pp. 38; dibenzalacetone and triphenylmethane, pp. 168; miscellaneous papers on aromatic compounds, pp. 90; miscellaneous papers on aliphatic compounds, pp. 38; nomenclature, pp. 10; sundry papers, pp. 17. The photogravure portrait of Baeyer, at the beginning of Volume I., is an excellent likeness and adds greatly to the value of the books.

Of the many reflections which these volumes suggest, two appear to call for special mention. Contrary to what one might have anticipated, Baeyer owed nothing of his success to family influence, indeed, as we have seen, he had to struggle against many difficulties, and suffer from lack of appreciation.

Like A. W. Hofmann, Bunsen, Würtz and other great leaders, Baeyer had laid the foundations of his fame at an age when many men are only just beginning to think of commencing graduate work.

Of his papers it will suffice to say that, for years past, a considerable number of them have ranked among the chemical classics. Their clear, lucid style, the simplicity and directness of statement, and the records which they contain of the wonderful technique and experimental skill of their author alike testify to the master mind and hand.

All true chemists will join with the reviewer in offering their most respectful congratulations to Professor Baeyer on this happy method of celebrating his birthday, and in expressing

their sincere desire that he may long be enabled to continue his contributions to the further advancement of the science he loves so well.

J. BISHOP TINGLE.

DIE TIERISCHEN GIFT. By EDWIN S. FAUST. Braunschweig: Friedrich Vieweg und Sohn. 1906. Price, M. 6.

The progress of knowledge in regard to the animal poisons is well illustrated by the inclusion of Dr. Faust's monograph in the series of "Die Wissenschaft" which, hitherto, has been devoted to monographs in the physical and chemical sciences. This distinction is entirely justified by a more exact knowledge of the animal poisons which has come, on the one hand, from their biological study, and on the other, from the application to them of those physiological-chemical methods which the last decade has seen so greatly defined. It is interesting to consider the very important part which the study by medical biologists of the phenomena of immunity has taken in advancing our knowledge of the chemistry of this class of poisons. Since the discovery of the peculiar reactions of the animal body which are now included generally under the term of "immunization," a valuable method has been discovered for establishing with accuracy identity or dissimilarity in many animal poisons. Even in cases in which the physiological reactions of the body to the poisons are not sufficiently distinctive to decide the question of relationship, the production of immunity in animals is often capable of deciding the doubtful results. It has been found that many of the animal poisons, belonging to a class of substances which chemically are difficult to define, produce, upon successive inoculation into animals, their antibodies. The latter are neutralizing in nature and are specific for the type of poison for which they have been developed. Thus, should animals be immunized with several kinds of snake venom, or poisonous blood sera, the resulting immune sera would be neutralizing for those poisons in venom or in serum with which the original poisons were in constitutional accord. By this means it has been possible to define chemically, with a considerable degree of accuracy, a number of animal poisons of which physiological studies alone had not entirely shown the relationship.

The complexity of many of the animal poisons, as brought out by this study, is often very great. To continue with venom as an illustration, it has been ascertained that of two venoms which produce similar effects on injection into animals, the effective poisons—say the blood-dissolving or hæmolytic and the nerve-destroying or neurotoxic poison—possess different chemical constitutions. We know nothing definite of the

ultimate chemical structure of these bodies, but by this "biological" reaction we can say, with confidence, that in spite of similarity of physiological effects a difference in chemical constitution exists. This knowledge, which must ultimately be of value to the organic chemist, may be somewhat disappointing to the medical investigator. Now that efforts are being made successfully to produce active antisera for vegetable and animal poisons which act injuriously upon and threaten the life of the higher animals, it adds greatly to the difficulties of the subject to be confronted with this tantalizing dissimilarity in the constitution of poisons, the physiological action of which is so much in accord. On the other hand, the value of the biological means of differentiation is enhanced by the very delicacy of the differences which it establishes.

Thus far chemistry, as such, has not succeeded in separating the animal poisons into their definite component parts and since these poisons have not, with very few exceptions, been obtained in states of purity, we are ignorant of their real nature. Even the term *toxalbumin*, which has been widely employed to designate them, is, in spite of its lack of definiteness, becoming more and more inapplicable as greater refinement of method removes from the poisons those obvious reactions upon which a belief in the albuminous nature of bodies has hitherto rested.

It will be impracticable in this review to do more than to indicate the subjects which are treated of in the present interesting compilation. After a general introductory chapter the poisons yielded by the class of vertebrata are discussed. Among the poisons which are considered are adrenalin, the poisonous crystalline principle of the suprarenal glands and the bile salts, all of which possess a high degree of toxicity. The larger part of the chapter, however, is devoted to the poisons yielded by snakes, the gila monster, the amphibia and fishes. More than half the book is devoted to this chapter. The remainder of the space is occupied with a description of the poisons yielded by the invertebrata—mollusks, arthropods, myriopods, insects, crustacea, worms, echinoderms and coelenterates. The literature has been carefully studied and a sufficient bibliography of the different subjects given. The treatment of the book is liberal and modern, and the author has indicated a grasp of the chemical and biological portions of his subject which shows a mastery of both.

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A HANDBOOK FOR CANE SUGAR MANUFACTURERS AND THEIR CHEMISTS. By GUILFORD L. SPENCER, D.Sc. New York: John Wiley and Sons. 1906. pp. vi + 203. Price, \$3.00.

The fact that this valuable handbook has passed to its fourth

edition shows the avidity with which it has been received by the technical sugar world. At the time the first edition was prepared there was grave question whether a book of its nature would find any remunerative sale. In the whole cane sugar producing world there were probably not a dozen factories employing chemists. When the book was published, however, it stimulated the desire among manufacturers of sugar cane to secure the chemical control therein described, and at the present time there is a markedly changed condition of affairs. There is scarcely a manufacturer of sugar, from the sugar cane, whose business is of any magnitude, who does not employ a chemist.

In addition to the chemists, who are directly interested, the book is useful to all who are concerned in chemical technology. It is a type of admirable treatment of a chemico-technical subject, both in character and in the arrangement of its contents. While the book is devoted principally to the description of chemical methods and chemical control, it is sufficiently explicit in its purely technical chapters to be of interest and value to the engineer. The apparatus and the manipulation thereof are described in detail, and this is followed by an account of chemical methods of research and the best means to employ for the most efficient control of a sugar house. Tables which are constantly used both by the engineer and the sugar chemist are appended to the body of the work, the whole forming a compact volume of convenient size.

H. W. WILEY.